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THE ELECTRON IN CHEMISTRY.*†

BY

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THE COMBINATION OF ATOMS TO FORM MOLECULES.

We shall begin by considering molecules in the gaseous state, where each molecule is separated so far from its neighbours that it may be regarded as an individual and not as merely forming a brick in a much larger structure. Indeed, the term molecule when applied to the solid state is quite ambiguous without further definition; for example, from many points of view we can consider quite legitimately the whole of a large crystal as forming a single molecule. It is natural to expect that when the atoms are crowded together as in a solid, where each atom may come under the influence of a large number of neighbours, the arrangement of the electrons relatively to the atom may differ substantially from that in a gaseous molecule.

Let us begin with the simplest case, that of the union of two similar atoms each containing one electron. We see that if the atoms and electrons are arranged as in Fig. 2, where A and B are the atoms and α and β the electrons, the mutual repulsion of the electrons may be balanced by the attraction of the positive charges on the electrons; and the mutual repulsions of the similarly electri-

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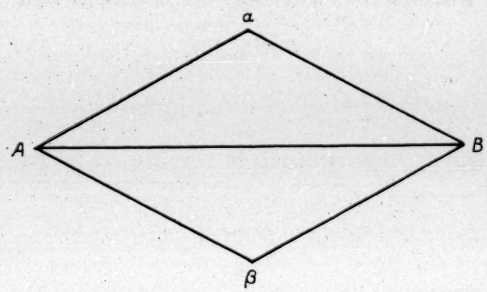
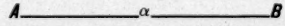
fied atoms by the attractions of the electrons. Thus we may regard the electrons in the atom as acting like hooks by which one atom gets coupled up with another. As the atoms are held together by the attraction of the pair of electrons α, β, the presence of two electrons between the atoms may be taken as the physical interpretation of what is called a bond by chemists. In

FIG. 2.



this example and in general, two electrons go to each bond. There are, however, cases such as that of a positively electrified molecule of hydrogen (so frequently detected in positive-ray photographs) where a single electron is able to bind two atoms together. The arrangement being that represented in Fig. 3.

FIG. 3.



The dimensions and shape of the parallelogram represented in Fig. 2 will depend on the law of force between two positive charges at atomic distances as well as upon that between a positive charge and an electron. If $e^2\varphi\left(\frac{c}{r}\right)$ is the attraction between a positive charge e and an electron with equal charge separated by a distance r and $e^2\psi\left(\frac{c^1}{r}\right)$ the repulsion between two positive charges at a distance r, then if $A\alpha = r$ and $< A\alpha\beta = \vartheta$, we have for equilibrium

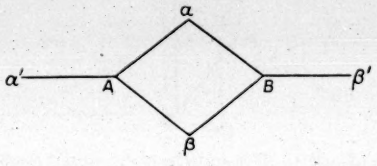
$$2e^2\varphi\left(\frac{c}{r}\right)\cos\vartheta = \frac{e^2}{4r^2\cos^2\vartheta} \qquad (25)$$

$$2e^2\varphi\left(\frac{c}{r}\right)\sin\vartheta = e^2\psi\left(\frac{c^1}{2r\sin\vartheta}\right)$$

Though the distance of an electron from its atom will obviously be not quite the same in the molecule as in the atom, we should expect that the differences would not be very large. For if they were, work would have to be done at some stage in the act of combination comparable with that required to ionise an atom, as this work is much greater than the equivalent of the heat developed by the union of the atoms to form a molecule we could not expect atoms under these conditions to combine to form molecules except in the presence of a very efficient catalyst.

Let us now pass to the case where each of the atoms contains two electrons. If only one pair of electrons is used up in uniting

FIG. 4.



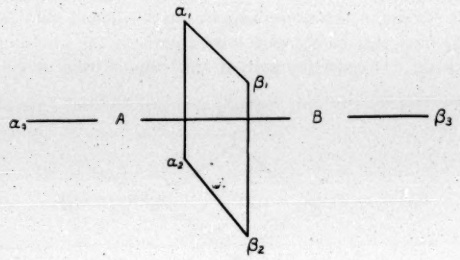
the atoms, the arrangement would be that represented in Fig. 4, where the Greek letters represent the electron. In the language of chemists this would be expressed by saying that the atoms were united by a single bond and the molecule would be expressed by the formula $-A-B-$. The electrons α' and β' would enable this molecule to link up with other molecules so that it would not be saturated. If, however, all four electrons are used in coupling up the atom, they will be at the corners of a square bisecting AB at right angles.

The system of four electrons instead of two between the positively electrified atom may be regarded as the physical equivalent of what the chemists call a double bond. Inasmuch as the equilibrium of four electrons in one plane, when their displacements are not confined to that plane, requires very strong restoring forces to make it stable, we should not expect the double bond to be permanent when the positive charges which exert the restoring force are as small as in this case, where their sum is only equal to the sum of the charges on the four electrons.

For the union of two tri-electron atoms, if all the electrons were used to couple up the atoms, there would be a hexagonal ring

of electrons in a plane bisecting AB at right angles, as this ring requires a greater positive charge than that of three units on each side to keep it in stable equilibrium it would be unstable. The most probable arrangement of the electrons is the octahedral one shown in Fig. 5 with four electrons between the atoms and two on the line AB; this would be represented symbolically by

FIG. 5.

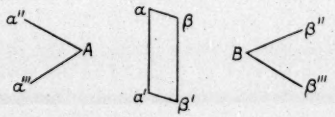


the formula $-A=B-$. The end electrons would enable it to bind other atoms so that the molecule would not be saturated.

FOUR-ELECTRON ATOMS.

These may form a molecule in which the electrons are as represented in Fig. 6, four electrons are between AB and the other four form two pairs beyond the extremities of the line AB.

FIG. 6.

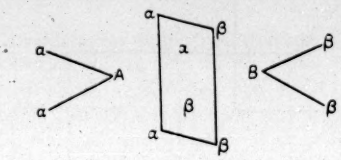


A peculiarity of the arrangement in Fig. 6 is that the molecule has four free electrons the same as the original atom, thus other atoms can be coupled up with the molecule, and we might have a chain of atoms, each atom being at the centre of a parallelipiped of eight electrons. We can show that a long chain of such atoms would be unstable, but it is evident that the four-electron atom is one peculiarly suited for forming

complexes containing several atoms. The carbon atom has four electrons in its outer layer and thus carbon atoms would have a great tendency to unite with each other. It is this tendency that is responsible for the Science of Organic Chemistry. I may point out in passing that we can obtain from the study of positive rays direct evidence of the coalescence of carbon atoms. For on a positive-ray photograph of benzene I found lines corresponding to C_1, C_2, C_3, C_4, C_5, where C_1 represents a carbon atom; C_2, a carbon molecule; C_3, a carbon triplet, and so on.

The form we have suggested for the electrons in the molecule of atoms of this type is represented symbolically by the formula

FIG. 7.



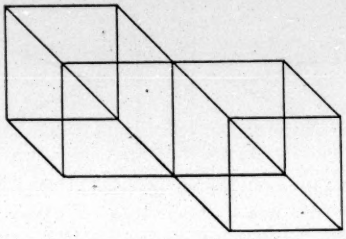
$= A = B =$. When we come to the case of five-electron atoms we have to introduce new considerations. We have seen that eight is the maximum number of electrons which can be in stable equilibrium in a single layer under the action of positive charges whose aggregate cannot exceed the total charges carried by the electrons. With a five-electron atom we have ten electrons in the molecule, while the aggregate positive charge, in the molecule, is also ten, which is not sufficient to keep the ten electrons in stable equilibrium if spread over a single layer. A simple way of arranging the electrons is shown in Fig. 7. Midway between the positive charges are six electrons which keep the atoms together, four of them at the corners of a square forming the normal double bond, while two others are inside the square.

The remaining four electrons are arranged in pairs beyond the atoms *A*, *B*, respectively. Thus we have eight electrons surrounding two atoms and two electrons. The arrangement is somewhat like that suggested for the carbon molecule with the addition of two electrons near the centre of the molecule.

When each of the atoms contains six electrons the arrangement is as follows: There are four electrons forming the normal double bond between the atoms, and two other sets of four, one

set beyond A, the other beyond B. Thus each of the two atoms may be regarded as being inside an octet of electrons, the two octets having four electrons in common. When each of the atoms contains seven electrons, we have fourteen electrons at our disposal. These may be arranged so that two of them form a single bond between the atoms while the remainder complete two octets with two electrons common to both, as is represented in Fig. 8. This, though a very symmetrical arrangement, is not the only conceivable one. For when the positive charges are large, as they are in this case, they might hold four or even more elec-

FIG. 8.

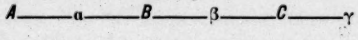


trons in stable equilibrium, even though the electrons were very close together. Thus suppose there were a double instead of a single bond between the atoms, this would account for four electrons, leaving ten to be distributed outside. If these were distributed symmetrically, there would be five around each atom, so that each atom would be the centre of a layer containing nine electrons, four coming from the double bond and five from those left over after the double bond has been provided for. Now nine electrons could not be in equilibrium if equally distributed under a central charge of seven, but if four of them are held close together in stable equilibrium under two positive charges, it is possible that there may be room for the other five to be so far apart that they can be kept in stable equilibrium by a positive charge of seven units.

It will be noticed that the molecules formed by the union of two atoms, each of which contains less than five electrons, have free electrons which are available for linking up with other mole-

cules. The one-electron atoms could form chains as in Fig. 9. Thus the process of aggregation is not exhausted by the formation of the molecule; these molecules will form further aggregations and thus tend to get into the solid or liquid state. On the other hand, the molecules formed by atoms with five or more electrons form saturated systems and will not tend to aggregate further. This agrees with the properties of the elements; for Li, Be, Bo, and C, whose atoms contain less than five electrons, are solids, while N, O, F and Ne, whose atoms contain five or more electrons, are gases.

FIG. 9.



From the consideration of the arrangements of the electrons in different molecules, we see that for the atoms containing four and five electrons we can regard the electrons in the molecule as roughly distributed over a single layer not very far from spherical, when, however, we reach the six-electron atom the electrons in the molecule form two cells, and a surface which would contain them all would have to be very elongated. We get some confirmation of this result from the study of the scattering of polarised light by gases. The theory of such scattering shows that the light scattered by a single electron in a direction at right angles to the incident beam is completely polarised and can be extinguished by a Nicol prism. The same thing is true when the light is scattered by a perfectly symmetrical body such as a sphere. If the scattering body is not perfectly symmetrical, if, for example, it is elliptical instead of spherical, the scattered light is never completely polarised and therefore cannot be entirely quenched by a Nicol. The ratio of the minimum to the maximum intensity of the light seen through a Nicol would be zero for a spherical body, but would be finite for an ellipsoid and would increase with the ellipticity. The value of this ratio may be taken as an indication of the deviation of the scattering body from sphericity. The scattering of light by molecules is due to the electrons in the molecules; we should expect that an arrangement of electrons in one shell would approach more closely to the spherical arrangement than an arrangement in two cells, and that two cells would approximate to the spherical more closely than three. Thus the

ratio of the minimum to the maximum intensity of the scattered light should increase with the number of cells. Lord Rayleigh[8] has determined the value of this ratio for several gases with the results given in the following table:

Gas.	Ratio Expressed as a Percentage.
Argon	.46
Hydrogen	3.83
Nitrogen	4.06
Oxygen	9.4
Carbon Dioxide	11.7
Nitrous Oxide	15.4

We see how small this ratio is for the symmetrical distribution of electrons round the argon atom. A striking feature of the table is the great jump between nitrogen and oxygen. We have seen that the passage from nitrogen to oxygen corresponds to the transition from an arrangement of the electrons in one cell to one in two cells, and thus involves a great loss in symmetry. The electrons in carbon dioxide and nitrous oxide require three cells for their arrangement and thus are less symmetrical than those in the oxygen molecule.

COMBINATION OF DIFFERENT ELEMENTS, CHEMICAL COMPOUNDS.

We may apply considerations similar to those we used to explain the formation of molecules of an element by the union of two similar atoms to the union of two different atoms to form the molecule of a compound.

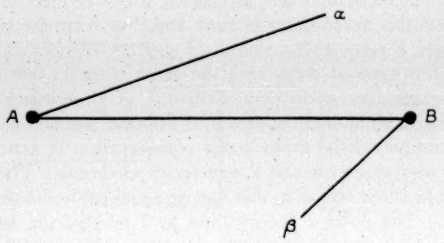
Let us consider, for example, the union of a seven-electron atom with a one-electron atom. Suppose that A is the centre of the first atom, B that of the second.

Let α be an electron in the first atom, β one on the second. Then if B and β place themselves somewhat as in the figure, the attractions the two electrons exert on A, B may keep these together in spite of their mutual repulsions, while the electrons are kept in equilibrium by the attraction upon them of the atoms A and B. The addition of β to the seven electrons already round A will raise the number in the outer layer of A to eight. Now suppose we attempt to attach another atom β' to A, this would introduce another electron into the outer layer round A, raising the number

[8] *Proc. Roy. Soc.*, **98**, p. 57.

in this layer to nine. We have seen, however, that nine electrons in one layer cannot be kept in stable equilibrium by a positive charge of nine units; in this case nine units are all we have at our disposal and two of these are outside the layer. The outside ones will make the arrangement of electrons more stable than it would be in their absence. They will not, however, increase the stability more than they would if they were inside, and even in that case they could not make the arrangement stable. Thus A cannot hold

FIG. 10.



a second atom of the type B, so that the compound AB_2 is impossible and that represented by AB is saturated. Thus, if B with its one electron is taken as the type of a monovalent atom, like hydrogen, A with its seven electrons would also be monovalent, and would in this respect act like fluorine. The electrons in the molecule HF would form a layer round the centre of the fluorine atom with the positive part of the hydrogen atom outside. Let us now suppose that A is a six instead of a seven-electron atom and let an atom of B get attached to it in the way we have supposed. This will raise the number of electrons in the layer round A to seven, so another atom can be attached before the number of electrons in the outer layer is raised to eight and the limit of stability reached. Thus A could form the unsaturated compound AB and the saturated one, AB_2, but A could not combine with more than two atoms of B. Thus A with its six electrons would behave like the atom of a divalent element, say oxygen.

In a similar way we see that if A contained five electrons it would form the unsaturated compounds AB and AB_2 and the saturated one AB_3. Thus A would behave like a trivalent element, nitrogen.

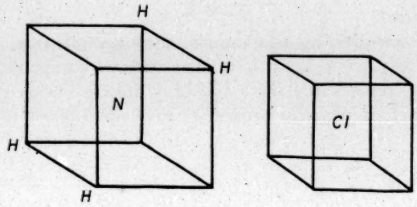
In this way we see that when A acts as the centre round which the layer of electrons is arranged, it behaves like an element whose valency is equal to (8 – number of electrons in the outer layer of the atom A).

There is, however, another way in which the atoms might combine, in this A, instead of receiving electrons from other atoms, might give up its electrons to help to form a layer round another atom. Take, for example, a two-electron atom B, by using one of its electrons it can attach itself to a seven-electron atom and still have one electron free. It can use this free electron to bind itself to another seven-electron atom and thus form the compound BF_2, where F represents an atom of such an element as fluorine. Thus in this type of compound the atom with its two electrons would behave like a divalent element. A three-electron atom would be able to bind three atoms of fluorine and so on. In this type of compound the atom under consideration is acting, so to speak, as a giver and not as a receiver of electrons. The valency of the atom when acting in this way is equal to the number of its electrons. The electron theory thus, as I pointed out long ago,[9] leads in a very natural manner to an explanation of valency and it suggests conclusions very similar to those advanced by Abegg and Bödlander,[10] who ascribed to each element two valencies according as it was combined with a more electronegative or more electropositive element. The sum of the two valencies always being eight. We have in some of the elements notable examples of two valencies; take nitrogen as an example, whose atoms contain five electrons in the outer layer. If this combines with hydrogen, three atoms of hydrogen will saturate it, as they will bring the number of electrons in the layer round the nitrogen up to eight, the limiting number, thus in the compound NH_3, the nitrogen behaves as a trivalent element. But suppose that instead of combining with a hydrogen atom it combines with a chlorine one, which we assume to have seven electrons in the outer layer. One of the electrons from the nitrogen atom might join the layer round the chlorine one, bringing the number of electrons in the latter up to eight, and leaving four in the nitrogen atom. These four electrons can link up with four hydrogen atoms which will bring the number of electrons in the layer round the nitrogen atom

[9] *Phil. Mag.*, [6] **27**, p. 757 (1914).
[10] *Zeit. Anorg. Chem.*, **20**, p. 453 (1899); **30**, p. 330 (1904).

up to eight, the limiting number. We thus get the compound NH_4Cl. The arrangement of the electrons being as represented in Fig. 11. As the chlorine nucleus has a positive charge of seven and is surrounded by a layer containing eight electrons, the atom Cl in this compound has a unit negative charge. Since there is a positive charge of five on the nitrogen nucleus and one of four on the four hydrogen atoms, there are nine positive charges on the system NH_4, which contains eight electrons;

FIG. 11.



there is thus a balance of one positive charge on the system represented by NH_4, so that NH_4Cl would, when electrolysed, give NH_4 and Cl as ions.

Again each of the five electrons of the nitrogen atom might go off to complete the tale of eight electrons round each of five chlorine atoms forming the compound NCl_5; though this substance does not seem to have been prepared, the corresponding compound PCl_5 is well known. The oxygen atom containing six electrons might attach itself to six atoms of chlorine and so be apparently hexavalent, as sulphur is in the remarkable compounds SF_6, discovered by Moissan.

Carbon having four electrons in the outer layer has the same valency $4 = 8 - 4$, whether it is acting in either of the above-mentioned ways, hence the compounds CH_4, CCl_4. The kind of union between atoms which we have been considering requires two electrons to effect the bond, hence since we cannot have more than eight electrons round a central atom, four is the maximum number of atoms which can be bound by a single atom. There are in fact very few exceptions to this rule, the most conspicuous are the chlorides of some of the elements which have very variable

valencies, such as $UrCl_5$ WCl_5, $MoCl_5$, which will be considered later.

Thus the considerations we have been discussing give a physical basis for the theory of valency in the extended form given by Abegg. The electron theory, however, is much more general than the laws of valency and points to the existence of compounds which are not in accordance with these laws. The electron theory states that any distribution of atoms and electrons in stable equilibrium is a possible compound and will be saturated provided that each electronegative atom is surrounded by a layer containing eight electrons.

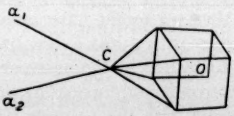
Let us consider, as an example, carbon monoxide, CO; this, according to valency laws, is an unsaturated compound, the gas is, however, remarkably inert and only liquefied with great difficulty, so that its physical properties give no support to the view that it is a highly unsaturated gas. In CO there are ten electrons to be arranged the same as in N_2, and we may therefore expect that a similar arrangement to that represented in Fig. 7 would furnish a stable and permanent molecule. As the positive charge on the carbon is not the same as that on the oxygen, the cell will not be so symmetrical as that of the nitrogen molecule. It is interesting to note that, as Langmuir has pointed out, some of the physical properties of CO are very similar to those of N_2. If this is the constitution of the molecule of CO, it explains why we do not get CH_2 as a saturated substance, as the ordinary valency theory would lead us to expect. There are only six available electrons in CH_2 and these are insufficient to produce a completely saturated layer. It is important to point out that we distinguish between the molecule of carbon monoxide and that of the carbonyl radicle CO.

In the latter we suppose that two out of the four electrons of the carbon atom have gone to unite it with the oxygen and to make up the eight electrons required to form the layer round the oxygen atom, while the other two are free to join up with other electrons. Thus while the molecule of CO is represented by Fig. 7, that of the carbonyl radicle is represented by Fig. 12.

Another molecule which may have a somewhat similar constitution to that of CO is NO, Fig. 12a. The molecule contains eleven electrons, if we take eight of these to form the outer layer we are left with three, these by taking up positions between the

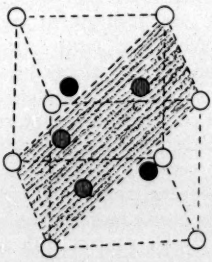
atoms of nitrogen and oxygen inside the outer layer may help to keep these atoms together. The molecule of nitrogen monoxide is not the only form in which the combination NO occurs; it can also exist as the radicle NO, and just as we suppose the carbonyl radicle to have a different configuration from that of the molecule CO, so we suppose that the radicle NO has a configuration in

FIG. 12.



which eight electrons form a cell round the oxygen, the nitrogen atom is surrounded by a layer of seven electrons made up of the three electrons left over after two have been supplied to the oxygen octet; the other four form part of the layer round the oxygen atom. The layer round the nitrogen requires another electron to saturate it and will thus act like a univalent atom. The

FIG. 12a.



three electrons left over from the five nitrogen electrons after two have been used to saturate the cell round the oxygen atom might be used to bind three hydrogen ions and thus it is possible that under certain circumstances this radicle might be trivalent.

Nitrogen monoxide is an example of the rare type of molecule where the number of electrons in the molecule is odd. Other examples of this type are NO_2 and ClO_2. If we suppose that for stable substances an octet of electrons is formed round each

of the heavier atoms in the molecule, then if the number of electrons is odd, some of these octets must have an odd number of electrons, either one or three, in common. If we suppose the octets are cubes, they could not have three electrons in common, though they could have one, the two cubes having a corner in common. If, however, the electrons are arranged in twisted cubes instead of the ordinary cubes, two octets might have 1, 2, 3 or 4 electrons in common, since twisted cubes have triangular as well as square faces and thus we might have molecules containing an odd number of electrons with a less exiguous connection between the atoms than that furnished by a single corner common to two octets. The three-electron contact would account for the existence of a saturated compound with the formula ClO_2. We have here nineteen electrons and these might be accommodated in three octets if there was one double contact and one triple one.

Another problem in which the triple contact might come in, is the well-worn one of the benzene ring. In benzene C_6H_6 we have thirty electrons which have to be arranged in octets round six carbon atoms. The simplest and most symmetrical way of doing this is to have the six cells in contact round a ring with a three-fold contact between each two. As two opposite triangular faces of the twisted cube are inclined to each other, this could be done without introducing much strain into the system. Models have been made by two of my students on this principle of a benzene ring and also of a naphthalene one. With this arrangement we have complete symmetry, and it is analogous to the Armstrong and Bayer or central theory of the benzene ring. The configuration corresponding to Kekules' conception of the constitution of the benzene ring would consist of three sets of pairs of cells, the cells in one pair having four-fold contact with each other, but only double contact with a cell in a neighbouring pair.

The three-contact view leads to results with regard to the constitution of addition compounds of benzene and the halogens which are in harmony with experience.

The process which we have just been describing by which two atoms A, B are united into a molecule AB, of a compound may be regarded as consisting in one or more of the electrons in the outer layer of A becoming a member of the outer layer of B. This is equivalent to one of the electrons in the outer layer of B

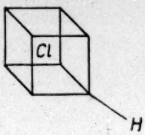
becoming a member of the outer layer of *A*. Thus each atom lends electrons to the other to enable it to fill up its outer layer; the atoms share their electrons for this purpose and the electrons which they have in common tend to hold the two atoms together. I think it is desirable to emphasize this aspect of the question, to regard the union of the two electrons as a sharing of their electrons rather than as the robbery of one atom of the electron belonging to another. I doubt if there is any very large change produced in gaseous compounds by chemical combination in the distance of an electron from the centre of the atom to which it originally belonged. I do not mean that the distance remains unaltered, but only that there is no such change in distance as would warrant our saying that the electron was bound to *B* before combination and was free afterwards. To tear electrons from an atom requires a much larger amount of work than to separate a molecule into uncharged atoms, and though there may be a redistribution of the electric charges on the molecule, there is nothing which can fairly be described as ionisation. Thus to take a specific example we regard the constitution of a molecule of HF as consisting of a unit positive charge H outside an outer layer of eight electrons surrounding the fluorine atom with its positive charge of seven units, and though we may legitimately describe the molecule as consisting of a positively charged hydrogen atom and a negatively charged fluorine one, it does not follow, if the molecule were dissociated by a rise in temperature, that the product of dissociation would be a positively charged hydrogen atom and a negatively charged fluorine one. It would take much less energy to detach the positive hydrogen atom plus an electron than the positively charged hydrogen atom alone, so that the probable result of the dissociation would be a neutral hydrogen atom and a neutral fluorine one. This would not necessarily be the case if the dissociation were effected by a high-speed positive ray with an energy corresponding to many thousand volts, for then the hydrogen atom could receive energy far more than sufficient to detach it from the negative electron. The result to which we have been led that dissociation would yield neutral atoms is in accordance with experience, for we do not find that chemical changes in gases produced by a rise in temperature are accompanied by a rise in electrical conductivity unless the gases are in contact with hot metals, and in this case the increase in conductivity may be explained by ther-

mionic effects. The absence of electrical conductivity in several cases of chemical action at moderate temperatures was investigated by Bloch,[11] who showed that the dissociation of arseniuretted hydrogen which takes place at low temperatures is not accompanied by any increase in the electrical conductivity. He also showed that many chemical actions which go on at low temperatures such as the oxidation of nitric oxide, the action of chlorine on arsenic, the oxidation of ether vapours, have little or no effect on the conductivity.

POLAR MOLECULES.

Though in the gaseous molecule we have not ionisation in the sense that the atoms of the molecules are free to move in opposite

FIG. 13.



directions under the action of an external electric force, yet the disposition of the electric charges may be such that the molecules would tend to set in a definite direction under the action of such an electric force. The centre of the positive charges does not always coincide with that of the negative ones, so the molecule may have a definite electric moment. It is only in some type of molecules that this electric moment has a finite value. Thus in the symmetrical molecule formed by the union of two atoms of the same kind the centres of the positive and negative electric charges coincide and the molecule has no electrical moment. Whereas in a molecule like HCl, where the positive charge is outside the octet as in Fig. 13, the molecule has evidently a finite electric moment.

In other compounds such as CO_2, of which the arrangement is that in Fig. 14, there is complete symmetry. Thus, as I pointed out some years ago,[12] molecules may be divided into two types: (*a*) Polar, those having a finite electric moment; (*b*) Non-polar, those for which the electrical moment vanishes.

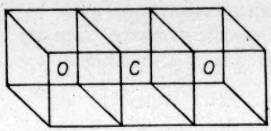
[11] *Ann. de Chimie et de Physique*, **22**, pp. 370, 441; **23**, p. 28.
[12] *Phil. Mag.*, **27**, p. 757 (1914).

These two types will have very different properties. If the molecule has a finite electrical moment, it will give rise to an electric field whose intensity will vary inversely as the cube of the distance, while if the electric moment vanishes the force due to the molecule will vary inversely as some higher power of the distance and will thus die away much more rapidly than the forces due to a polar molecule; the latter will have a more extensive stray field and will attract and be attracted by a much larger number of other molecules.

PHYSICAL TEST FOR POLAR MOLECULES.

We shall first describe a test based on physical principles by which we can separate the polar from the non-polar molecule and

FIG. 14.



then see whether the molecules so separated show marked difference in their chemical properties.

The physical method for determining whether the molecule has a finite moment or not is the determination of the specific inductive capacity of the substances formed by the molecules, and if possible when the substance is in the gaseous state. The molecule with a finite moment will tend to set in a definite direction under the electric field, and this setting will contribute to the specific inductive capacity of the gas, hence such molecules will tend to give an abnormally high value to the specific inductive capacity. Again, since this setting of the molecule involves the rotation of the molecule as a whole, these will move so sluggishly that they will not be affected by vibrations as rapidly as those of light waves in the visible spectrum.

Hence these molecules will not affect the refractive index in the visible spectrum while they will affect the specific inductive capacity. We should expect, therefore, that the substances formed by such molecules would depart widely from Maxwell's law that

the square of the refractive index is equal to the specific inductive capacity. Again, since the setting of the molecules under the electric field will be hampered by the collisions with other molecules and as these collisions are more numerous and vigorous at high temperatures than at low, the specific inductive capacities of these substances will be affected by temperature and will diminish as the temperature increases. Bädeker [13] has determined the specific inductive capacities of many gases at varying temperatures, and it appears from his results that some of these gases, such, for example, as H_2O, NH_3, HCl, CH_3OH, exhibit all these characteristics, they have specific inductive capacities which are much greater than the square of the refractive index and which diminish as the temperature increases.

Taking this as the criterion, we can find whether the molecules have or have not finite electrical moments and in the following tables, derived from measurements made by Bädeker and other observers, of the specific inductive capacity of gases, various compounds are placed in one or other of two classes.

TABLE I.

Compounds which have a finite electrical moment.

H_2O	CH_3OH
NH_3	C_2H_5OH
SO_2	CH_3Cl
HCl	$CHCl_3$ (slight)

TABLE II.

Compounds which have not a finite electrical moment.

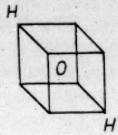
H_2	CO_2
O_2	CS_2
N_2	CCl_4
He	C_6H_6
Cl_2	CH_4
CO	N_2O

This list shows that the physical test we have applied separates the substances into two types which have great differences in their chemical properties. In the first type we have substances like water and alcohol which are good ionisers of salts or acids dissolved in them.

[13] *Zeit. fur Physik Chem.*, **36**, p. 305.

The substances in the first table are also those which, like water, ammonia, and alcohol, are conspicuous in forming complex compounds with other salts, such as the hydrates, alcoholates, ammoniates. Another property which differentiates the substances in Table I from those in Table II is that of giving electrification by bubbling. When air or other gases bubble through some liquids, *e.g.*, water, alcohol, acetone, the gas when it emerges is found to be ionised, *i.e.*, mixed with positive and negative ions. Little, if any, electrification is found when a gas bubbles through a liquid like paraffin oil or benzene. This is shown very clearly

FIG. 15.



by the experiments of Bloch.[14] Liquids of the first type show electrification by bubbling, those of the second do not.

Molecules which contain the hydroxyl radicle OH, such as H_2O, CH_3OH, C_2H_5OH, are usually polar; other organic radicles, such as COOH, CO, CN, NO_2, also make the molecules of which they form a part polar. As the attraction of polar molecules extends over a much wider field than that of non-polar ones, we can understand why, though the hydrogen in saturated non-polar molecules such as CH_4, C_2H_6 is not oxydised by weak solutions of sulphuric acid or bichromate of potash, the hydrogen in polar molecules such as CH_3OH, CH_2O (formaldehyde), CHOOH, is oxydised under the same conditions.

The fact that the polar molecule must be unsymmetrical gives us some information about the configuration of the electrons. One of the most interesting cases is that of water, which is conspicuous above all molecules for the possession of an electrical moment. Our first impression is that the structure of the water molecule should be that represented by Fig. 15, where the two hydrogen atoms are symmetrically placed with respect to the centre of the oxygen atom and the electrons are symmetrically distributed round the line joining the hydrogen atoms. This, how-

[14] *Ann. de Chimie et de Physique*, **23**, p. 28 (1911).

ever, cannot be right, for it would correspond to a molecule having no electrical moment. If the octet of electrons round the oxygen atom were situated at the corners of a cube, then there could be no question that a symmetrical arrangement of the hydrogen atoms with these atoms, respectively, attached to two electrons at the opposite ends of a diameter would be the position of equilibrium and this would correspond to a system having no electrical moment. If, however, the electrons were arranged at the corners of a twisted cube, no two electrons would be at opposite extremities of a diameter. Thus, if the positive atoms were attached to two electrons the system would be unsymmetrical and would have an electrical moment. Thus the electrical and chemical properties support the view that the electrons in the octet are at the corners of a twisted cube. The symmetrical position for the hydrogen atoms would, with the twisted cube, be when the positive hydrogen atoms are on the axis through the centre at right angles to the square faces. On this axis the positive atoms cannot be at a distance from the nearest electron less than half the diagonal of a square face. This distance is greater than would be necessary if the hydrogen atoms were placed close to the corners of the octet. This increase of distance would correspond to an increase of potential energy which might make the arrangement unstable. It would appear from these considerations that there may be more than one form of water. Thus the two hydrogens might be joined (*a*) to two electrons on the same square face or (*b*) one of the hydrogens might be joined to an electron on one square face and the other hydrogen to an electron on the other. Similar considerations would apply to the hydroxides of the alkali metals, but we should hardly expect the want of symmetry in these to be as pronounced as in hydrogen for the reason that the radius of say an atom of sodium is greater than that of one of hydrogen, so that these atoms might be able to get into the symmetrical positions without their distance from the nearest electron being increased much beyond that between the atom and electron in the uncombined atom. The effect of increased size may be illustrated by comparing water with methyl ether, which may be regarded as water in which the hydrogen atoms are replaced by the larger CH_3 group. The specific inductive capacity of methyl ether and its dissociating power are very much smaller than those of water.

As another instance of the aid which considerations like these

may give in determining the structure of the molecule, we may take the case of SO_2. The determination of its specific inductive capacity shows that it has a finite electrical moment. It is therefore more likely to be represented by one of the unsymmetrical formulas S – O – O, O – S – O, than by the more symmetrical one

A molecule of a gas with a large electrostatic moment may itself promote combination between two gases, neither of which has molecules with a finite moment. Let us consider the effect of a molecule of this kind on the molecules of a gas near it. The intense electric field around this molecule will drag towards it the molecules around it; it will act as a nucleus round which the molecules of the other gas will condense. The nucleus will thus bring these molecules nearer together than they otherwise would be, and if like chlorine and hydrogen they can combine the presence of the nucleus, will assist combination. It seems possible that part of the action of water vapour in chemical combination may arise in this way, the interacting molecules crowding together so as to get into the strongest part of the electric field round the water molecules and thus getting into positions which are favourable for chemical combination.

In some cases the product of the chemical action will be active molecules with large moment. This will happen in the case of hydrogen and oxygen, or with hydrogen and chlorine, since the molecules of water and hydrochloric acid have a finite electrostatic moment. Here chemical combination promoted by the water vapour produces a fresh supply of active molecules and thus of nuclei which promote the combination. There will evidently be a tendency for mixtures of this type to become explosive. It is the intense electric field round a molecule with a finite electrostatic moment which causes the other molecules to condense round it. If, instead of a molecule with its electrostatic doublet, we had a charged ion, we should have a still more intense electric field and therefore might expect to get still greater condensation and more intense chemical action. The study of the conduction of electricity through gases gives us evidence of the existence of this condensation, as the ions in gases behave more like clusters than single molecules or atoms. It may be asked why is it that while

molecules possessing finite electric moments are able to promote so markedly chemical action, yet the speed of these actions is not noticeably greater in ionised than in non-ionised gases, though in the former the ions must produce intense electrical fields? The answer to the question is, that in any ordinary type of ionisation the number of charged ions is very small indeed compared with the number of molecules of a foreign constituent of the gas, even when the constituent is present as the merest traces. Take, for example, the case of water vapour, if the partial pressure of the water vapour were only the millionth of an atmosphere there would still be about 2.8×10^{13} molecules of water vapour per cubic centimetre. With such ionising agents as Röntgen rays, it is exceptionally strong ionisation when there are 10^{10} ions per cubic centimetre, so that even with the amount of water vapour mentioned above, which it would be very difficult to avoid, even with the most careful drying, there would be about 2800 times as many molecules as there are ions in an intensely ionised gas. In cases where there are an exceptionally large number of ions present as, for example, in the negative glow in a discharge tube, all kinds of chemical actions seem to go on with great facility.

We shall see later on how these polar molecules are able to bring about dissociation of salts in liquids as well as promote chemical action.

It can be shown [15] that if M is the electrostatic moment of a molecule, *i.e.*, the product of one of the charges into the distance between the charges in an electric doublet which would produce the same electrostatic effect as the polar molecule; then K, the specific inductive capacity of the gas at the absolute temperature T and at a constant density corresponding to that at 760 mm. pressure and 0° C., is given by the equations

$$K = a + \frac{.88M^2 \times 10^{36}}{T} \tag{26}$$

where a is independent of the temperature. Hence measurement of K at two different temperatures would give us M.

Applying this formula to the results of Bädeker's experiments, I find that for water

$$M = 2.1 \times 10^{-18} \tag{27}$$

for ammonia

$$M = 1.5 \times 10^{-18} \tag{28}$$

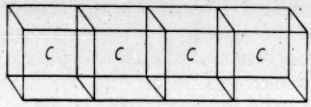
[15] *Phil. Mag.*, **27**, p. 763 (1914).

It is probable that determinations of K, and thereby of M, at different temperatures for different gases, would give us valuable information as to the lack of symmetry in the molecules of the gas.

ARRANGEMENT OF ELECTRONS IN OCTETS.

We have seen that when a shell of electrons surrounds a positive charge equal to the total charge on the electrons so that the system as a whole is electrically neutral, eight is the maximum number of electrons which can be in stable equilibrium on the shell. If some of the positive charge be taken from the inside of the shell and placed outside in symmetrical positions so as not to destroy the approach to sphericity of the shell of elec-

FIG. 16.



trons, we can prove that though this transformation will increase the radius of the shell, it will not in general increase the stability, and that eight will still be the maximum number of electrons which can, consistent with stability, be on the shell.

Thus confining our attention to systems such as those formed by collections of atoms where there is no excess of one kind of electricity over the other, eight will be the maximum number of electrons that can be included on a single spherical surface, while, if there are less than eight, the system will not be saturated. It follows from this that any system of electrons and atoms which is stable and saturated must consist of a number of cells of electrons, each cell containing eight electrons and having a charged atom inside. It does not follow that all configurations which can be built up in this way are possible, for though each cell might be stable if all the electrons and positive charges outside it were fixed, yet an aggregate of such cells need not be stable if all the electrons and atoms can move quite freely. Thus we cannot be sure that all distribution of electrons into octets represents a possible compound—as a matter of fact, we know that many do not. Thus to take a system of octets like that shown in Fig 16,

which represents a line of cubes placed face to face, each cube containing a positive charge equal to four. This is an electrically neutral system, and corresponds to a long line of carbon atoms. This system turns out on mathematical investigation to be unstable and therefore a long chain of carbon atoms cannot exist, but would break up into shorter chains, each containing 2, 3 or 4 atoms; this is in accord with chemical experience. On the other hand, long

FIG. 17.

chains of the radicle CH_2 exist in many organic compounds. I have found that the analogous system consisting of a row of doubly charged positive atoms, each of which is at the centre of a tetrahedron of electrons as in Fig. 17, is stable. Take, as another example, a long row of cubes placed edge to edge as in Fig. 18, each cube containing a positive charge 6, this would form an electrically neutral system and would correspond to a long chain of oxygen atoms. The mathematical theory, however,

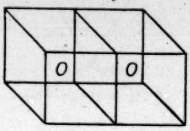
FIG. 18.

shows that this arrangement is unstable and this is confirmed by experience as compounds which contain even very short chains of oxygen atoms are highly explosive.

This division into octets may be regarded as a kind of entrance examination which every candidate for recognition as a formula representing the structure has to pass, and not as being necessarily either the right or even a possible formula. It is a necessary condition which every formula must fulfil, but it is not sufficient to ensure the stability of the compound. It was just the same on the old theory of valency; all kinds of compounds could be imagined which would satisfy the valency condition, but only a small fraction of these have been detected. In fact, chemistry is something more than freehand drawing.

If we wish to find any arrangement of octets which can represent a molecule consisting of specified atoms, we have to solve the following problem. The number of electrons at our disposal is known because we know the atoms of which the molecule consists; we know the number of cells because there is to be one round each of the atoms which in a free state have four or more electrons in the outer layer. Thus we know the number of cells required and the number of electrons at our disposal; we have to see if it is possible to arrange the electrons in octets. If the octets were separate and did not go shares in any electrons, each cell would require eight electrons. Whenever we make an octet share an edge with another, we save two electrons; if it shares

FIG. 19.

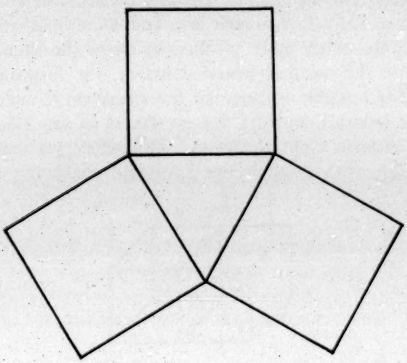


a triangular face, we save three; if it shares a square face, we save four. We have to try to find contacts between the octets of such a kind that the saving of electrons will equal the difference between eight times the number of cells required and the number of electrons at our disposal. Thus to take an example, suppose we want the arrangement for two oxygen atoms; here two cells are required and there are twelve electrons at our disposal; we have therefore to save four electrons by the contact between the two cells; to do this the octets must have a square face in common, so that the only possible arrangement is that represented in Fig. 19.

Suppose, however, we have three oxygen atoms to arrange in a molecule; hence we require three cells and we have eighteen electrons at our disposal; hence we have to save $3 \times 8 - 18 = 6$ electrons by the contacts. We may do this in two ways: In one represented in Fig. 20, we have three line contacts, at each of which two electrons are saved. In the other, we have that represented in Fig. 21, where we have one line contact, saving two, and a face contact saving four. The first arrangement is represented by , the second by O = O – O; which are

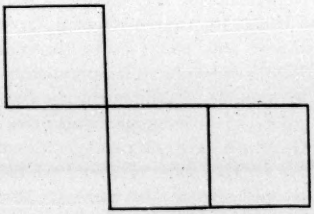
two possible formulas for ozone. If both are possible, there must be two kinds of ozone; the first of these being quite symmetrical would represent a molecule without a resultant electric

FIG. 20.



moment, the second we should expect to involve a finite moment. As we can detect the existence of electrostatic moments by experiment on specific inductive capacity, we may hope to find out

FIG. 21.

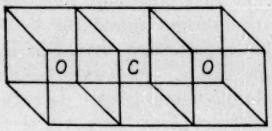


whether or not there are two kinds of ozone and, if there is only one, which is the formula which represents its constitution.

For CO_2 we require three cells, and we have $4 + 2 \times 6 = 16$ electrons. We have, therefore, to save $3 \times 8 - 16 = 8$ electrons by the contacts; if the atoms are in a line there are only two of these, hence we have to save four at each contact, so that the

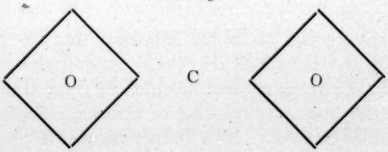
configuration will be that represented in Fig. 22. This configuration can also be regarded as a quadruply charged carbon atom placed midway between two oxygen atoms surrounded by octets of electrons, each of these systems carrying a charge −2, the molecule being represented by $\underset{-2}{O}=\underset{4}{C}=\underset{-2}{O}$. We may point out that we might have another configuration for the same distribution of electric charges, *viz.*, that represented by Fig. 23; here the

FIG. 22.



oxygen atoms carry the same charge as before, but they present an edge of the octet to the carbon atom instead of the full face. In this case we see that the layer of electrons nearest the carbon atom only contains four electrons, in that represented in Fig. 22 it contains eight. Thus this layer is saturated with the arrangement of Fig. 22, but not with that of Fig. 23. Thus if the electrons in CO_2 were arranged as in Fig. 23, the molecule

FIG. 23.



would not be saturated; it could accommodate, for example, two molecules of water if these were arranged so that the water octet presented an edge to the carbon. While if they were arranged so that each of the water octets presented a point to the carbon atom instead of an edge, it could accommodate four molecules of water. If the oxygen atom also turned a corner to the carbon atom instead of an edge, there would be accommodation for six molecules of water. We thus see that where there are contacts such as those in Fig. 22, which are represented by double bonds

between the atoms, we can, by altering the orientation of the cells, make room for other neutral molecules or radicles. The whole number of system nearest to the central atom must not, however, exceed eight.

DISPOSITION OF THE ELECTRONS IN TYPICAL COMPOUNDS.

Chlorides.—Monochlorides, type HCl. We have here a positive charge outside the octet. The compound has a finite electrostatic moment. The region around the hydrogen atom is comparatively free from electrons, thus molecules of water could be held in stable equilibrium round the hydrogen ion, so that substances with this composition should be hygroscopic.

Bichlorides, type $CaCl_2$. A double positive charge between two octets; the molecule is non-polar. If each of the octets presents a face to the calcium atom, there will be eight electrons on a sphere round this atom; with this configuration there is no room for other molecules. If the chlorine octets swing round so as to present an edge instead of a face to the calcium atom, there will only be four electrons on the layer next to this atom. Thus there would be room for two water molecules if the water octets came edge foremost, or for four if they came point foremost. While if the chlorine octets were also point foremost to the calcium atom, there would be room for six molecules of water. We should expect these chlorides to be very hygroscopic.

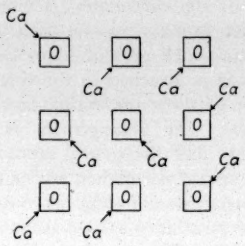
An interesting fact about the halides is that we find chlorides such as tungsten hexachloride, WCl_6, and molybdenum pentachloride, $MoCl_5$, sulphur hexafluoride, SF_6, in which there are more than four atoms of chlorine or fluorine combined with one atom of another element. Now if each octet is to present an edge to the central atom, it will furnish two electrons to the layer round the central atom and as the number of electrons in this layer cannot exceed eight, it follows that there cannot be more than four atoms of one kind combined with one of another, a rule to which there are a few exceptions, such as these we are considering. We may explain the existence of these in two ways—one is to suppose that only four of the chlorine atoms are in the inner zone, that the other two are in the outer zone. In this case two chlorine octets carrying a negative charge would be easily detached, so that the compound should be a good electro-

lyte. The other supposition is that all the chlorine octets are in the inner zone, but only two of them present an edge to the central atom, the other four only presenting a corner. The difference between the two is roughly that on the first supposition, two chlorine octets are loosely and four firmly held, while on the second two are firmly and four loosely held.

Oxides.—The points previously raised in connection with water apply to the oxides of the univalent elements generally.

Oxides of divalent elements of the type CaO. Here we have

FIG. 24.



the core of the calcium atom outside the oxygen octet. If this octet presents an edge towards the calcium atom, there will be room for three more octets, each presenting an edge, so that we can easily understand why this substance dissolves easily in water. It is not necessary that the octets which go to complete the tale round the calcium atom should be those of water molecules, they may be the octets of other CaO molecules. The fact that the octet of one molecule of CaO can also find its way into the inner zone surrounding other Ca atoms, will have a great effect in binding the different molecules together and thereby account for the very high melting points of the oxides. The arrangement in two dimensions when molecules of CaO mutually saturate each other is shown in Fig. 24. The arrow between Ca and O indicates that two electrons have gone from this particular calcium atom to complete the octet round the oxygen atom. The octets are supposed to present their edges to the calcium atom.

Sesquioxides, type B_2O_3. The most symmetrical arrangement for oxides of this type would seem to be one where the three oxygen octets have their centres at the corners of an equivalent

triangle, while the cores of the two boron atoms are symmetrically placed on an axis at right angles to this triangle and passing through its centre.

Carbonates.—M_2CO_3. We have here three oxygen octets surrounding a central carbon atom. If the inner zone round this atom is to be saturated with electrons, one of the octets must turn a face, while the other two octets present edges, towards the carbon atom. If the octet turning its face to the carbon twists round and turns an edge, there will be room for another octet in the inner zone; thus the molecule can take up water or bind itself to other molecules of the carbonate. There would seem to be the possibility of two isomers, in one both the metal atoms are attached to the octets which present edges to the carbon; in the other, one metal atom is attached to the octet presenting a face and the other to one of those presenting an edge.

Nitrates.—MNO_3. The arrangement is the same as for the carbonates, except that the central atom is nitrogen, with a positive charge of five and not carbon with a charge of four, and there is only one metal atom instead of two to put outside the octets. There is the possibility of two isomers as before.

Sulphates.—M_2SO_4. Here we have four oxygen octets surrounding a central sulphur atom. These must have edges and not faces turned towards this atom. As all the four octets are turned the same way and are similar there will be no isomers.

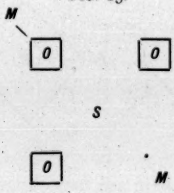
Perchlorates.—$MClO_4$. The same as the preceding, except that the central atom is chlorine and not sulphur, and there is only one metal atom to place outside the octets.

Sulphites.—M_2SO_3. These from our point of view differ from the carbonates and nitrates because after providing for the electrons to furnish the three oxygen octets, there are still two electrons to provide for. The most symmetrical way would be to arrange them as in Fig. 25, *i.e.*, with one of the M atoms connected directly up with the sulphur and not indirectly through an oxygen octet. This would put the metal atom in the inner zone, from which we should not expect it to be detached in electrolysis; thus if M were hydrogen, this arrangement would correspond to a monobasic acid. H_2SO_3 is, however, dibasic and therefore has probably both the H atoms connected directly with the oxygen and not with the sulphur. In this case we see that there are two electrons which have no direct connection with any

but the sulphur atom, and which would be available for attaching to the M_2SO_3 molecule the positive part of any polar molecule or to complete the octet of an oxygen atom and thus form the sulphate.

Chlorates.—$MClO_3$. Here we have the same number of electrons as in the sulphites, but the fact that the chlorates very readily give up oxygen while the sulphites take it up, suggests a

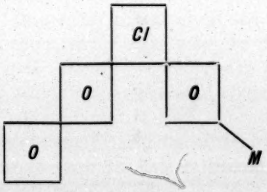
FIG. 25.



different grouping of the electrons. The arrangement given in Fig. 26, where one of the oxygen atoms is bound to another oxygen atom and not directly to the chlorine, would represent a molecule which would readily part with oxygen.

This arrangement of two oxygen octets with an edge in common is one that occurs in connection with the molecules of

FIG. 26.

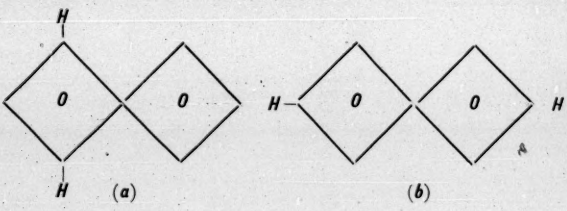


exceptionally intense oxidising agents, and we have already met with it when considering the form of the molecule of ozone. In hydrogen peroxide H_2O_2 there are two possible forms, one represented by Fig. 27: (*a*) In which both hydrogen atoms are attached to the same oxygen octet, and the other (*b*) when one hydrogen atom is attached to one oxygen octet and the other to the other. In both cases we have two oxygen octets connected together by an edge. The first one would possess a finite electrical

moment, the second one would not, so that the forms could be distinguished by measuring the specific capacity of H_2O_2 in the gaseous state.

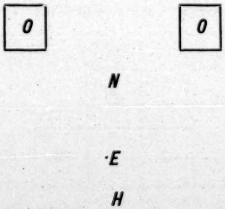
Nitrites.—HNO_2. The nitrites resemble the sulphites in having two electrons which are not in direct connection with any

FIG. 27.



but the central atom. There are two oxygen octets and two electrons *E*, as in Fig. 28. If the hydrogen ion took up the position (H), it would be bound by these electrons, the hydrogen would be in the first zone and the substance would not be an acid. If

FIG. 28.



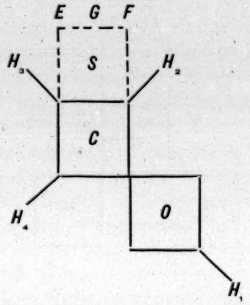
the hydrogen is attached to one of the oxygen octets, the substance will be an acid, and the two electrons will be free to complete the octet round a neutral atom of oxygen, link it up with the nitrogen, and convert the nitrite into a nitrate.

CONNECTION BETWEEN CHEMICAL CONSTITUTION AND CHEMICAL PROPERTIES.

If we know the distribution of the electrons and positive charges in a molecule, the behaviour of the molecule under specified physical conditions can be calculated from the forces

exerted on each other by the electric charges. The exact calculation in most cases would be a process of considerable length, but we can get without an appreciable amount of mathematics a general idea of the nature of the change in properties likely to be produced by changes in the composition of the molecule. The clearest way of illustrating the point in question is to take an example. Methyl alcohol CH_3OH is a substance without any tinge of acid properties; in fact, it is basic, if anything. When,

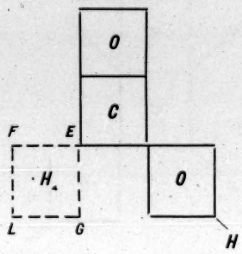
FIG. 29.



however, two of the hydrogen atoms are replaced by an oxygen one we get formic acid, a substance with pronounced acid properties. We know the general character of the distribution of electrons in the two cases, can we see why the difference in the distribution should make the difference betwen an acid and a feeble base? We shall suppose that the acid character of a substance containing the hydroxyl radicle OH depends on the ease with which the hydrogen ion H can be detached from the oxygen. We have therefore to see what is the difference between the force on the hydrogen ion in CH_3OH and CH.O.OH. The arrangement of the electrons in methyl alcohol is represented in a general way by the continuous lines in Fig. 29, where for the sake of avoiding confusion in the drawing, the tetrahedral arrangement of the H_3, OH atoms round the central carbon atom has been replaced by an arrangement in one plane. We have the octet round the carbon atom; the size of this does not vary much from one compound to another. We may thus regard this octet as occupying much the same position

in the formic acid as in the methyl alcohol. Consider the difference when we replace two of the hydrogens H_2, H_3 by an atom of oxygen. We take away the positive charges H_2H_3, and replace them by a positive charge 6 at the centre S of the oxygen octet, and four negative electrons at the corners E,F of the face of this octet. Thus the difference between the forces on the atom H_1 in the hydroxyl radicle in the methyl alcohol and formic acid is the difference between the force exerted by the positive charge 6 at S, by the four electrons on the face EF of the octet, and

FIG. 30.



that exerted by the two positive charges H_2H_3, which can be represented approximately by a positive charge 2 at S. Subtracting this from the charge 6 due to the oxygen, we see that the change due to substituting the oxygen for the two hydrogens can, as far as the forces are concerned, be represented by a plus charge 4 at S, and a charge on the whole amounting to -4 carried by four electrons at the corners of the square face of the octet. If we replace these by a charge -4 at G, the centre of the square face, then the force on H_1 in the formic acid molecule will equal the force on H_1 in the molecule of methyl alcohol plus the force due to the doublet with a positive charge 4 at S and a negative one -4 at G. The effect of the doublet is, as will be seen from the figure, to repel H_1 away from O. It will thus tend to detach H_1 from the molecule, *i.e.*, to make the molecule act like an acid.

As a further example let us consider whether replacing a hydrogen atom in such a compound as formic acid by a chlorine one would increase or diminish the acid properties of the molecule.

Suppose that Fig. 30 represents the distribution of the

electrons in a molecule of formic acid. If the hydrogen H_4 were replaced by chlorine, the change as far as the electrical forces are concerned will be that the charge +1 at H_4 will be replaced by a charge +7 carried by the chlorine atom, and that six other electrons will be introduced which, with the two along the edge E, will make up the octet round the chlorine atom. To calculate the effect of these six electrons, we take the four along the edges F and G; these are at the corners of a rectangle whose centre is at S, the centre of the chlorine atom. If these electrons act as if they were concentrated at the centre of figure S, they will have the effect of reducing the positive charge at the centre of the chlorine atom from 7 to 3. Now take the two electrons at the edge L; these with two of the three charges at the centre of the chlorine atom will form an electrical doublet whose moment is $2e \times LS$ with its positive part turned towards the centre of the molecule, the remaining positive charge at S will represent the positive charge on the hydrogen atom before it was replaced by chlorine. Thus the difference in the forces due to the replacement of hydrogen by chlorine is represented by the electrical doublet $2e.LS$, and this as we see from the figure will tend to drive off the hydrogen in the hydroxyl radicle—thus the substitution of chlorine for hydrogen tends to increase the acidity of the molecule. This is very strikingly shown by monochlor, dichlor and trichlor acetic acids, which are much stronger acids than acetic acid itself.

It follows from the investigation we have just given that if in a hydrocarbon such as CH_4 we substitute for one of the hydrogen atoms E, the atom of an electronegative element such as chlorine, the change in the electric forces can be represented by the introduction of an electrostatic doublet at E with its axis along CE and the positive part of the doublet turned towards C. The molecule of CH_4 before the substitution of the chlorine atom was non-polar, *i.e.*, the molecule had no electrostatic moment, the substitution of the chlorine for the hydrogen introduces a finite electrostatic moment and thus makes the molecule polar.

The positive part of the doublet at E is turned towards C, hence the force it produces at F, G, H, the other corners of the tetrahedron whose centre is at the carbon atom, will tend to attract negatively and repel positively charged atoms. Hence if a molecule of CH_3Cl were placed under such conditions that there

were positively and negatively charged atoms in its neighbourhood, the concentration of the negative atoms round *F, G, H* would be greater than it would be for the molecule CH_4 before the hydrogen at *E* had been replaced by the electronegative chlorine. Thus the substitution of the atom of an electronegative element for one of the hydrogen atoms round the carbon will tend to promote the substitution of electronegative atoms for the remaining hydrogen atoms. If two of the hydrogen atoms are replaced by an atom of oxygen, this will for the same reason promote the substitution of electronegative atoms for the other two hydrogen atoms. We have illustrations of this effect in the following examples for which I am indebted to Mr. W. H. Mills.

Ethyl chloride + chlorine (1 molecule) in the liquid state under the influence of ultra-violet light,

$$CH_3 . CH_2Cl \longrightarrow \underset{70 \text{ per cent.}}{CH_3 . CHCl_2} + \underset{10 \text{ per cent.}}{CH_2Cl . CH_2Cl}$$

Ethyl bromide heated with bromine in sealed tube,

$$CH_3 . CH_2Br_2 \longrightarrow CH_3 . CHBr_2$$

Chlorine on boiling toluene ($C_6H_5.CH_3$) in sunlight gives successively

$$C_6H_5CH_2Cl,\ C_6H_5CHCl_2,\ C_6H_5CCl_3$$

We see from these examples that there is a tendency for a new hydrogen atom to go into that part of the molecule which is already halogenated.

In the presence of catalysts such as ferric bromide, the halogen atoms in the higher members of the series go to the carbon atom adjacent to the one already brominated.

Another illustration of this effect is the well-known fact that when an organic compound is oxidised the carbon atom attacked is the one which already is attached to oxygen.

I pass on now to consider a problem which I can best explain by stating a particular case. Why is it that in a compound such as methyl alcohol $H_3C.OH$ the only atom of hydrogen which is replaceable by a monovalent metal is the one in the hydroxyl radicle. Or to take another aspect of the same problem, why can the hydrogens in marsh gas not be replaced by the monovalent positive elements, while they can be replaced by the monovalent negative ones like Cl, Br, I? Let us consider what are the conditions for the existence of CH_4. We have an octet of electrons

round the carbon atoms. The carbon atom which only carries a charge of four units could not by itself keep eight electrons in stable equilibrium. It is enabled to do this by the stabilising effect of the positive charges which are on the hydrogen atoms. This stabilising effect will depend on the distance of the positive charge on the hydrogen from the nearest electron in the octet, a distance which we should expect to be not greatly different from the radius of the hydrogen atom. Consider now the effect of replacing the hydrogen atom by one of an alkali metal; the radius of the atom of the alkali metal is very considerably greater than that of the hydrogen atom. The control over the electron in the metal is much less than that on the electron in the hydrogen atom. This is shown by the fact that the ionising potential for the hydrogen atom is much greater than that for the metal one, thus we should expect the stabilising effect of the positive part of the metal atom to be very considerably less than that of the hydrogen atom. Thus while the stabilising effect of the hydrogen atom may be great enough to make the octet of electrons round the carbon atom stable, that of the metal atom may not be able to do so, in which case the metallic compound could not exist.

In this view the atoms of the monovalent metals are not efficient stabilisers of an octet of electrons, and we should expect that in the compounds they form the octet should be of a kind that requires little help from the positive charge on the metal atom to make it stable.

Let us consider a few types of the salts formed by these monovalent metals. Let us begin with the chlorides, here we have an octet of electrons round the chlorine atom and the positive charge outside. Now experiments with positive rays show that a neutral chlorine atom, having seven electrons in the outer layer readily takes up a negative charge, *i.e.*, acquires another electron. Thus an octet of electrons round a chlorine atom is stable even without the assistance of an external positive charge, and thus a metal atom outside an octet round a chlorine atom will be a system where the octet is very stable. Hence we should expect that all these alkali metals would, as in fact they do, form chlorides readily. Now let us turn to the hydroxides. The neutral hydroxyl radicle has seven electrons arranged round the oxygen atom. Now again experiments with positive rays show that the hydroxyl radicle very often occurs with a negative charge and in

this state there must be an octet of electrons round the oxygen atom. Thus such an octet with the hydrogen atom outside is stable by itself even without assistance from the positive part of a metallic atom. Thus when it gets this assistance the octet will be very stable, so that we should expect, as in fact is the case, that the hydroxides of the alkali metals would be formed very readily.

Now let us turn to the oxides, here we have an octet round the oxygen atom and the positive part of two metallic atoms outside. As lines corresponding to negatively electrified oxygen atoms are to be seen on nearly every positive-ray photograph, a system of seven electrons round the oxygen atom must be a stable system. In the case of the metallic oxides we have two positive charges to make the system stable when another electron is added. We have seen from the case of hydroxyl that a single hydrogen atom is able to bring about this stability, so that as two metal atoms are available the metal atoms would have to be very inferior to the hydrogen one as stabilisers if the octet were not fairly stable.

Now let us consider why it is that, while we cannot replace by a metal one of the hydrogen atoms directly connected with the carbon atom in a hydrocarbon, we can replace the hydrogen in a hydroxyl group linked up to the carbon. Let us take methyl alcohol as an example, where we may suppose the electrons are arranged as in the diagram. We see that from its position the hydrogen in the hydroxyl group has little to do with the stability of the octet round the carbon atom; it is the stability of that round the oxygen atom with which it is concerned. Now an octet round an oxygen atom is a very different thing as far as stability is concerned from one round a carbon atom. We have seen that seven electrons can be in stable equilibrium round an oxygen atom without any help from systems outside and that a single positively charged hydrogen atom outside is sufficient to make the octet stable. If the hydrogen in the hydroxyl is replaced by a metallic atom, then to keep the octet round the oxygen atom stable we have not only the positive part of the atom of the metal, but also that of the carbon atom with its attached electrons and positive hydrogen atoms. Thus the conditions are much more favourable for the stability of this octet than they are for that round the carbon atom, and thus it may be possible to replace the hydrogen in the hydroxyl but not that in the rest of the atom.

The positive rays afford evidence that to make the octet of electrons round the carbon stable in a compound CH_3X, where X is a monovalent element, assistance is required from X. For if it were not, the system got by removing the positive part of X would be stable, but this system is just the radicle CH_3 with a negative charge. Now the line corresponding to this radicle occurs frequently in positive rays, but always with a positive charge, while other radicles, such as OH, are found with negative as well as with positive charges. This is an indication that the stability of the octet round the carbon atom depends upon the presence of X. On the other hand, if the residue after taking away an atom of hydrogen from a hydrocarbon is stable even after receiving a negative charge we should expect that the hydrogen atom might be replaced by an atom of the metal, for the molecule is stable after the hydrogen has been removed and the octet does not depend on the positive charge for its stability. Now on many positive-ray photographs I have observed a line corresponding to a molecule with a negative charge, whose molecular weight is 25, when hydrocarbons were in the discharge tube. The molecular weight indicates that the molecule is C_2H, *i.e.*, acetylene minus an atom of hydrogen, if this is so the hydrogen in acetylene might be replaced by a metal: The compound C_2Cu_2 which is of this type is well known.

Though we have seen the stability of the oxides indicates that the octet round the oxygen atom can be stabilised by the presence outside it of the positive parts of metallic atoms, there are indications that this octet is not so stable as those in the chlorides and hydroxides. The main evidence is that many oxides and sulphides when in the solid state are conductors of electricity, especially at high temperatures, and that, as the researches of Königsberger and Horton show, this conductivity is not electrolytic, but resembles that through metals. There are some chlorides which conduct in the solid state, but as far as I am aware their conductivity is always electrolytic. The conductivity of metals can, as we shall see, be explained as due to electrons which move freely about in certain directions through the solid. So that the non-electrolytic conductivity of these oxides and sulphides indicates that some electrons have got free, *i.e.*, that some of the octets round the oxygen and sulphur atoms have broken up. This breaking up increases very rapidly with the temperature. Another piece of

evidence to the same effect is the very intense thermionic emission by oxides such as those of calcium, strontium and barium, an emission which, as Horton has shown, is far more intense than that from the metals themselves at the same temperature. On our view this is due to the breaking up of the octets round the oxygen atoms. The smaller the charge on the neutral atom, the more will the stability of the octet round it depend on the positive charges outside. Thus as nitrogen has only a charge 5 while oxygen has one of 6, we should expect the octet round nitrogen in a metallic compound to be more easily broken up than that round oxygen in metallic oxides. It would be interesting to test from this point of view the properties of tripotassiumamide, NK^3.

RESIDUAL AFFINITY, MOLECULAR COMPOUNDS, WERNERS COÖRDINATION NUMBERS.

We have regarded the molecule of a chemical compound as made up of atoms some of which have lost electrons, while others have gained them, so that the former are positively, the latter negatively, electrified; the forces between the electrical charges on the atoms and electrons binding the atoms together in such a way as to form a stable system. The number of electrons which an atom can gain or lose depends upon the nature of the atom. The number it can lose is equal to the number of electrons in the outer layer, and varies from one to eight according as the element belongs to one or other of the Mendeleefian groups; the number it can receive is 8 minus the number in the outer layer.

If the transference of electrons has proceeded to its limit, *i.e.*, if every positively charged atom has received the maximum positive charge of electricity it can acquire and every negatively charged one its maximum charge of negative electricity, there must be simple relations between the number of different kinds of atoms in a neutral molecule. Thus, for example, if we have two kinds of atoms, *e.g.*, calcium and chlorine, since the neutral calcium atom has two electrons in its outer layer and the neutral chloride seven, the calcium atom can lose two electrons while the chlorine atom can only gain one. We see therefore that when the transference of electrons has gone as far as possible, each calcium atom will have given up its electrons to two chlorine atoms neither more or less and thus for each calcium atom positively charged

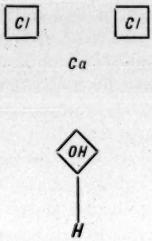
there must be two chlorine ones with negative charges, thus the composition of the molecule would be represented by the symbol $CaCl_2$. And we can show easily that when the transference of electrons has proceeded to the limit the proportion between the numbers of the various kinds of atoms in the molecule will be the same as that deduced from the ordinary principles of valency.

In such a molecule as $CaCl_2$ the transference of electrons has reached its limit, and as far as this property is concerned the molecule may be regarded as "saturated." Unfortunately there has been a tendency to regard this "saturation" as applying to quite a different thing. Some chemists have supposed not merely that the calcium atom when it had charged two chlorine atoms had exhausted its power of charging up any more atoms negatively, which is true, but they implied, which is not true, that the doubly charged calcium atom cannot by its attraction hold more than two atoms in stable equilibrium. It is important to distinguish between the maximum positive charge the atom can acquire and the maximum number of negatively electrified systems which the maximum charge can hold in stable equilibrium in a single layer around it. The table given in the first chapter shows that when the attractive force between the positive charge and a negative one is represented by $\frac{a}{r^2} - \frac{b}{r^n}$, the number of negative charges which a positive charge can hold in stable equilibrium in a single layer is, when the positive charge does not exceed a limit determined by the value of n, greater than the number of units of positive charge on the central system. This is confirmed by the fact that the positive-ray method reveals the existence of negatively charged atoms, for example, the atoms of hydrogen, carbon, oxygen, chlorine are frequently found to be negatively charged, and a negatively charged atom must have more electrons than the number of units of positive charge. Thus, though a calcium atom could not itself charge negatively more than two chlorine atoms, yet if a third chlorine atom, negatively electrified by some external agent, were brought near the calcium atom, it would hold it in stable equilibrium and form the system $\overset{+2}{Ca}\ Cl\ Cl\ Cl$. This system would, however, be negatively charged and so could not be expected to remain free under normal conditions; it might, however, be found in electrolytes or charged gases. There may, however, be electrically neutral compounds in which the calcium

atom is surrounded by more than two systems. Let us suppose that instead of bringing up a negatively electrified chlorine atom to the $CaCl_2$, we bring up a molecule which possesses considerable electrical moment, *i.e.*, one in which the positive and negative parts are separated by a considerable distance, such, for example, as a molecule of water $H(OH)$. The negative end of this would place itself closer to the calcium than the positive one and we should get a system such as that represented in Fig. 31.

This system as a whole is electrically neutral and so could exist

FIG. 31.



under normal conditions; it would be held together by forces of just the same type as those which hold the atoms together in $CaCl_2$, yet from the ordinary chemical point of view the latter is a valency compound while the former is not.

It must be noticed, however, that though the number of systems that can exist round the central atom may be greater than the positive charge on that atom, theory indicates that there is a sharp limit to this number, so that the possible compounds of this type would be determined by definite rules.

We can get some information about the number of atoms or molecules which can be grouped in stable equilibrium about a central system S by applying the condition for stability which we have already used when considering the stability of arrangements of electrons in the atom. Let us suppose that the atoms grouped around S are the centres of octets of electrons, the electrons in these octets which are nearest to S will furnish a layer of electrons round S and for stability the number of electrons in this layer must not exceed eight. The number of electrons an octet will supply to this layer will depend upon the orientation of the octet.

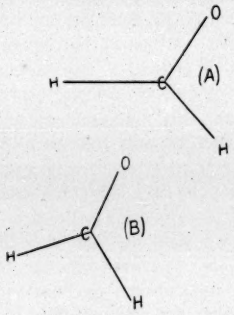
If O is the centre of the octet, then if SO passes through an electron, *i.e.*, if the octet presents a corner to S, it will supply one electron to this layer. If SO bisects at right angles the line joining two electrons on the octet, *i.e.*, if the octet presents an edge to S, two electrons will be supplied, while if SO is at right angles to a face of the octet, *i.e.*, if the octet presents a face to S, four electrons will be supplied. When all the octets present corners to S the maximum number around S will be eight. Considering the exiguous character of this connection between S and the octets, we should not expect this arrangement to have any very great stability. If each octet presents an edge to S, the maximum number of octets will be four, while if each presents a face to S, the maximum number will be two. Thus the number of systems which can be held in stable equilibrium in the first zone round S, which following Werner we shall call the coördination number of S, may vary from 2 to 8. Werner finds that an appreciable number of elements have a maximum coördination number four, a few have eight, the number for the majority is, however, six, which would correspond to four of the octets presenting a corner, and two an edge to S.

The coördination number is never less than the valency and is generally greater. The somewhat vague notion implied by the use of the term "Residual Affinity," which appears frequently in chemical literature, is an attempt to give expression to the facts implied by a difference between the valency and the coördination number. The consequences of this difference are of the first importance. Let us see, for example, how it would facilitate the aggregation of molecule. Let us take as an example formaldehyde COH_2, a substance which is saturated for valency purposes, but is not coördinately saturated. Thus if A (Fig. 32) represents a molecule of formaldehyde, then if the coördination number of carbon is four, A can hold another negatively electrified oxygen atom in its shell; this may form a part of another formaldehyde molecule B, and thus A and B may be held together in the way indicated in Fig. 32. As B is not coördinately satisfied, it may link up with the oxygen from a third molecule C; in this way aggregates of the formaldehyde molecule would be formed readily.

We can apply to the union of molecules considerations quite analogous to those we applied to the combination of atoms. Thus, for example, we can picture two molecules of Li Cl joined together

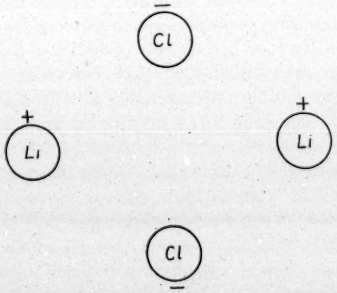
by an arrangement like Fig. 33, which is similar to that binding two atoms of lithium together, the electrons in the latter being replaced by negatively electrified atoms in the chloride. Indeed,

FIG. 32.



if the coördination number were always eight, the molecular compounds would run quite parallel with the atomic ones, *e.g.*, the atoms would be arranged in octets in the molecular compounds

FIG. 33.



just as the electrons are arranged in octets in the atomic ones. Since eight is the maximum number of electrons which can be arranged in one layer round a central atom, eight is the coördination number of an atom with respect to electrons; hence when the coördination number in molecular compounds is eight, we see

that the molecular compounds will run parallel to the atomic ones. Let us apply this result to a particular case. We saw that when the atoms of an element contain few electrons, so few that these are not sufficient in a diatomic molecule to make up the total of eight, the molecules have a great attraction for each other, so that the element under normal conditions is in the solid state, *e.g.*, Li, Be, Bo, C. When, however, there are sufficient electrons in the atom for the atoms in a diatomic molecule to make up, by sharing electrons, one or more octets, the molecules have but little attraction for each other, and the element is gaseous, *e.g.*, N_2, O_2, F_2, Ne. Considerations of exactly the same character will apply to the molecular compounds formed, for example, by the chlorides. A chloride like NaCl, which contains only one chlorine atom, is analogous to an atom containing only one electron; a chloride like $BeCl_2$, which contains two chlorine atoms, to an atom containing two electrons and so on. The molecules formed by atoms which contain less than five electrons exert great attractions on each other and condense into the solid state, while those containing five or more electrons are much more volatile and for the elements in the first period are gaseous. The result we have just obtained shows that we may apply to the chlorides the same reasoning as we applied to the atoms. Hence we should expect those chlorides which contain only a small number of chlorine atoms, to be solids; while those containing more than a certain number of chlorine atoms should be much more volatile. The following table of the boiling points of the different chlorides and fluorides shows that this is the case to a very marked extent.

The number of halogen atoms corresponding to a volatile or non-volatile substance will depend upon the coördination number of the element with which the halogen atoms are combined. The smaller the coördination number of the element, the smaller the number of chlorine atoms required to make the chloride volatile. As the coördination number varies from element to element, the connection between volatility and the number of chlorine atoms cannot be expected to be as clear cut as that between the volatility of an element and the number of electrons in the atom, when the coördination number of an atom with respect to an electron is always eight. The non-volatility of some of the chlorides such as WCl_5, WCl_6 is, I think, due to the chlorine atoms being in two layers, so that the number in the outer layer, which

Compounds Containing One Halogen Atom.

Name.	Formula.	Melting point.	Boiling point.
Sodium chloride	NaCl	776	
Silver chloride	AgCl	450	
Sodium fluoride	NaF	above 902	

Compounds Containing Two Halogen Atoms.

Calcium chloride	$CaCl_2$	720	
Magnesium chloride	$MgCl_2$	708	
Strontium fluoride	SrF_2	above 902	
Calcium fluoride	CaF_2	above 902	
Stannous chloride	$SnCl_2$	250	620

Compounds Containing Three Halogen Atoms.

Antimony trichloride	$SbCl_3$	73	223
Bismuth trichloride	$BcCl_3$	230	430
Boron trichloride	BCl_3	liquid	18

Compounds Containing Four Halogen Atoms.

Silicon tetrachloride	$SiCl_4$	liquid	50
Stannic chloride	$SnCl_4$	liquid	114
Titanium tetrachloride	$TiCl_4$	liquid	135
Silicon tetrafluoride	SiF_4	gas	

Compounds Containing Five Halogen Atoms.

Antimony pentachloride	$SbCl_5$	gas	
Molybdenum pentachloride	$MoCl_5$	194	268
Tungsten pentachloride	WCl_5	248	278

Compounds Containing Six Halogen Atoms.

Sulphur hexafluoride	SF_6	gas	
Tungsten hexachloride	WCl_6	275	346

determines the volatility, is less than the number of chlorine atoms in the compound.

Another example of the analogy in physical properties for similar proportions between the number of electrons in the atom and the number of chlorine atoms in a chloride is afforded by the consideration of the electrical properties of the elements and of chemical compounds.

When there are less than four electrons in the outer layer of an atom of an element, the element is a metal and a good conductor of electricity, the conductivity arising from the movement

of the electrons; when there are more than four electrons in the outer layer the element is a bad conductor of electricity. The electrical conductivity of fused chlorides may be compared with that of the metals, the negatively electrified chlorine atoms taking the place of the electrons and making the conduction electrolytic. Chlorides containing a small number of chlorine atoms are good conductors when fused, while the higher chlorides like $SnCl_4$, CCl_4 insulate, although they are in the liquid state.

The thermionic properties of metals find, too, a parallel in those of the chlorides. A metal contains lattices of positively electrified atoms and electrons, the solid chlorides, lattices of the atoms of the metal and of negatively electrified chlorine atoms, and the work required to eject a chlorine atom from the salt would be of the same order as that required to eject an electron from the metal. Again, the proportion between the number of atoms and electrons in the metal would be the same as that between the number of metal atoms and of chlorine atoms in its chloride. Hence we should expect from thermodynamic considerations that at temperatures at which the thermionic emission of electrons from the metal is considerable, there should be an emission of negatively electrified chlorine atoms from the salt. Such an emission does in fact take place.[16] When salts are first heated considerable currents are carried by the chlorine atoms and no electrons can be detected. The effects produced by prolonged heating are very complicated, more so even than those occurring on the emission of electrons from hot metals. This is what we might expect, as the tearing away of the chlorine atoms would produce a more fundamental change in the surface than the emission of electrons from a metal. After prolonged heating electrons, as well as chlorine atoms, are given off, suggesting that the tearing away of the chlorine atoms has produced an excess of metal atoms at the surface.

When the coördination numbers of the metals occurring in double salts are not all equal, the arrangement of the electronegative atoms round the atom of the metal will not be in octets, but one which provides a layer of negative atoms round each atom equal to the coördination number of that atom.

Before leaving the consideration of the coördination number we must raise the question whether a doubly charged atom like

[16] Richardson, "Emission of Electricity from Hot Bodies."

oxygen ought to count as two towards the coördination number as it does towards the valency. If we take the view before discussed, the oxygen atom for coördination purposes ought to count as one and not as two. On that view the limits to the coördination number depend on the octets round the central atom. An octet with a double charge, such as that associated with an oxygen ion, can be orientated so as not to bring more electrons into the layer next the central atom than an octet with a single charge like that associated with a chlorine ion, thus the oxygen need not count for more than the chlorine.

ELECTROLYTIC DISSOCIATION.

When the coördination number of the central atom is greater than its valency, the molecule can combine with polar molecules such as H_2O, NH_3 to form new compounds in which the atoms in the original molecule are driven further apart, and are therefore able to rearrange themselves with the expenditure of much less energy than would have been necessary if these compounds had not been formed. Positively and negatively charged atoms may in this way be thrust so far apart and the connection between them made so slight that they move in opposite directions under the action of an electric field, and are thus resolved into ions.

This is well illustrated by the well-known example given by Werner of the ammoniates of platinic chloride. If the coördination number of platinum is six, then in $PtCl_4$ there is room for two polar molecules in the first layer round the platinum atom without that layer becoming unstable. The chlorine atoms are in direct connection with a platinum atom and so cannot be detached easily from it. Thus the compound $PtCl_4(NH_3)_2$ is not an electrolyte. If, however, more molecules of NH_3 are added, since 6 is the maximum number of constituents which can be in one layer round the positive charge, the constituents in the inner layer must break up into two groups, one group forming a layer of six next the platinum, the remainder forming an outer layer at some distance from the inner one. The process is very closely analogous to that described in Chapter I when new layers of electrons were formed when the number of electrons in the atom exceeds the number which can be held in stable equilibrium in one layer by the central positive charge.

Thus if four molecules of ammonia are added to the platinic

chloride, there must be two constituents in the outer layer; if these are chlorine atoms carrying a negative charge they will be easily detached and form negative chlorine atoms and the compound will be, as Werner showed it is, an electrolyte, with ions $PtCl_2(NH_3)_2^+$ and $\overset{-}{Cl}$ $\overset{-}{Cl}$. The work required to separate the ions comes from the loss of potential energy due to the approach of the polar molecules to the central system, and not from thermal agitation. The reasons in favour of this view of electrolytic dissociation are in my opinion very strong. I have already pointed out that to ionise a molecule isolated from other molecules would require an amount of energy comparable with the "ionising potential" of one of its atoms, a quantity varying from one element to another, but comparable with 10 volts. As the average kinetic energy of a molecule at 0° C. due to thermal agitation is, when measured on the same scale, only about 1/30 of a volt, it will be seen that there is little likelihood of the ionisation being due to thermal agitation.

On this view of electrolytic dissociation the ions in the solution are not simple atoms or radicles, but combinations of these with polar molecules. These molecules not only dissociate the original molecule, but after dissociation they tend to keep the ions apart. They surround the charge on the central atom with an oppositely charged layer and thus diminish its attraction on other systems. Thus, for example, in an aqueous solution of $CaCl_2$ the positively electrified part of the calcium atom would have next to it the negative ends of polar water molecules, and the attraction between it and an oppositely charged chlorine atom would be diminished. The researches of Mr. Washburn furnish direct experimental evidence of the hydration of ions.[17]

(To be continued.)

On the Production of Colored Flames for Use with Spectrometers and Polarimeters. J. J. MANLEY. (*Phil. Mag.*, Feb., 1923.)—From the laboratory of Magdalen College, Oxford, comes this method of feeding the solution through a bunch of platinum wires into the flame. It seems to be a boon to physicists for "It is extremely convenient, requires but little attention and by its means an intense flame coloration can be maintained for any desired period." In addition it can be made by the experimenter. G. F. S.

[17] *Technology Quarterly*, 21, p. 288 (1908).

Hendricus Gerardus van de Sande Bakhuyzen, the Dutch astronomer, died on January 8, 1923. He was born in the Hague in 1838. After having been professor of physics in the Polytechnic School in Delft, he became professor of astronomy at the University of Leiden and director of the observatory. Under his direction a catalog of more than 10,000 stars was made. He worked with Gill, the Cape of Good Hope astronomer, to determine the amount of astronomical refraction. His study of changes of the mean level of the sea on the Dutch coast contributed to the explanation of variation of latitude. The period of the rotation of Mars was determined by him to a fraction of a second. Outside of his chosen field, he had a large part in the publication of the monumental edition of the works of Huyghens and he further served as secretary of the International Society of Geodesy. (*Comptes Rendus,* Jan. 22, 1923.)

G. F. S.

Spectra of Hydrogen, Nitrogen and Oxygen in the Extreme Ultra-violet. J. J. HOPFIELD. (*Phys. Rev.,* Dec., 1922.)—"It had long been assumed by investigators in the extreme violet, that most gases, and especially oxygen, are opaque in this region." Certain previous experiments made by this author had led him to doubt this. His present paper shows that he was correct. He used a vacuum grating spectrograph, specially prepared photographic plates and an oil-cooled discharge tube capable of standing an input of 2.25 KW. All three gases were found to transmit light of wave-length 1100 to 1225 Ångstrom units even when the pressure was as high as 3 cm. In oxygen at .001 mm. pressure its spectrum was photographed down as far as 430 units. The wavelengths of 100 new oxygen lines are given, obtained with the disruptive discharge. Fifty new nitrogen lines are also given.

G. F. S.

The Early Stages of a Submarine Explosion. (*Phil. Mag.,* Feb., 1923.)—Gas is supposed to be set free in an instant in a spherical cavity situated in a limitless mass of liquid assumed to be incompressible. If the diameter of the cavity is at first one metre and the initial pressure of the gas 1000 atmospheres, then in water the diameter doubles in $\frac{1}{250}$ sec. and grows to 5 metres in about $\frac{1}{80}$ sec. The maximum speed with which the limits of the cavity travel outward is 145 m. per sec., nearly one-tenth of the speed of sound in water. If the initial pressure had been 10,000 atmospheres, the doubling and the quintupling of the diameter would occur in respectively $\frac{1}{1800}$ and $\frac{1}{1100}$ sec., while the maximum outward speed would be 460 m. per sec.

The compressibility of water will, of course, modify these data, though to no great extent, until pressures of the order of 10,000 atmospheres are introduced. "The accurate equations of motions of spherical waves are easily formulated, although a solution seems at present hopeless."

G. F. S.

ILLUSTRATIONS OF ELECTRIC DISPLACEMENT CURRENTS.*

BY

JOSEPH S. AMES, Ph.D., LL.D.

Director of Physical Laboratory, The Johns Hopkins University, Baltimore, Maryland; Associate Editor of this JOURNAL, Member of the Institute.

THIS note contains a method of discussing displacement currents which is perfectly obvious and yet which, so far as I can learn, is not given in any text-book on electricity; and also a few illustrations.

If ε is the dielectric constant of a homogeneous isotropic dielectric and $\overline{E}$ the intensity of the electric field at any point in it due to any distribution of stationary charges, the electric displacement $\overline{D}$ at that point is defined by the equation $\overline{D} = \frac{\varepsilon}{4\pi}\overline{E}$. Maxwell introduced the concept of a displacement current, whose value per unit cross-section is defined to be $\frac{\partial \overline{D}}{\partial t}$, and discussed the continuity of the vector sum of the conduction current density $\overline{j}$ and $\frac{\partial \overline{D}}{\partial t}$. Later, as a consequence of Rowland's experiments on convection of electric charges and the resulting idea of convection currents, FitzGerald showed that $j + \frac{\partial \overline{D}}{\partial t} + \rho\overline{v}$, where ρ is the volume density of charge and $\overline{v}$ is its velocity, was the vector to be considered as the total current density. Various authors have shown, therefore, that this vector is to be considered as solenoidal.

As the simplest illustration of displacement currents, those due to a point charge e moving with a "slow" velocity v may be considered. Since this problem is obviously one of axial symmetry, the axis of X may be chosen as the direction of the velocity and that of Y any line perpendicular to this. An observer moving with the charge would observe in the space around him a potential $\varphi = \frac{e}{\varepsilon r}$, and values of the electric intensity whose components $E_x = -\frac{\partial \varphi}{\partial x}$, $E_y = -\frac{\partial \varphi}{\partial y}$, $E_z = 0$. An observer, stationary in space, will note the same values, provided the velocity of the charge is

* Communicated by the Author.

so slow that the electric intensity $\frac{1}{V}[v.H.]$ may be neglected. To this latter observer the displacement current density will have the components $\frac{\partial D_x}{\partial t} = \frac{\varepsilon}{4\pi}\frac{\partial E_x}{\partial t}$ and $\frac{\partial D_y}{\partial t} = \frac{\varepsilon}{4\pi}\frac{\partial E_y}{\partial t}$. But $\frac{\partial}{\partial t} = -v\frac{\partial}{\partial x}$, where x is the coördinate of the point in question with reference to axes moving with the charge. Therefore

$$i_x = \frac{\partial D_x}{\partial t} = -\frac{\varepsilon}{4\pi} v \frac{\partial E_x}{\partial x};$$
$$i_y = \frac{\partial D_y}{\partial t} = -\frac{\varepsilon}{4\pi} v \frac{\partial E_y}{\partial x}$$

A stationary doublet of strength ve, consisting of charges $+\frac{e}{\alpha}$ and $-\frac{e}{\alpha}$ at a distance αv apart, where α is an infinitesimal number, whose axis is taken as the axis of X, produces a field of displacement whose components at any point are

$$\frac{\varepsilon}{4\pi}\left\{E'_x - \left(E'_x + \frac{\partial E'_x}{\partial x}\alpha v\right)\right\} = -\frac{\varepsilon}{4\pi}\alpha v \frac{\partial E'_x}{\partial x} \quad \text{and}$$
$$\frac{\varepsilon}{4\pi}\left\{E'_y - \left(E'_y + \frac{\partial E'_y}{\partial x}\alpha v\right)\right\} = -\frac{\varepsilon}{4\pi}\alpha v \frac{\partial E'_y}{\partial x}$$

The E'_x and E'_y in these expressions are the components of the electrical intensity due to a charge $\frac{e}{\alpha}$; in the formulas for i_x and i_y, E_x and E_y refer to a charge e; therefore $E'_x = \frac{1}{\alpha}E_x$; $E'_y = \frac{1}{\alpha}E_y$. Finally, the field of displacement due to the stationary doublet of strength ve has for its components $-\frac{\varepsilon}{4\pi} v \frac{\partial E_x}{\partial x}$ and $-\frac{\varepsilon}{4\pi} v \frac{\partial E_y}{\partial x}$, identically the same as the components of the displacement current density due to a charge e having a velocity v.

This theorem may be generalized: Let there be any distribution of charges, ρ, σ or e, which has a uniform velocity $\overline{v}$; the displacement current density produced thereby is identically the same as the displacement due to a stationary polarized distribution formed by associating with $\frac{\rho}{\alpha}$, $\frac{\sigma}{\alpha}$ or $\frac{e}{\alpha}$ charges of opposite signs at a distance αv in a direction opposite to that of the original motion. This fact enables one to draw the lines of the displacement current density immediately, if the corresponding lines of displacement are known.

ILLUSTRATIONS.

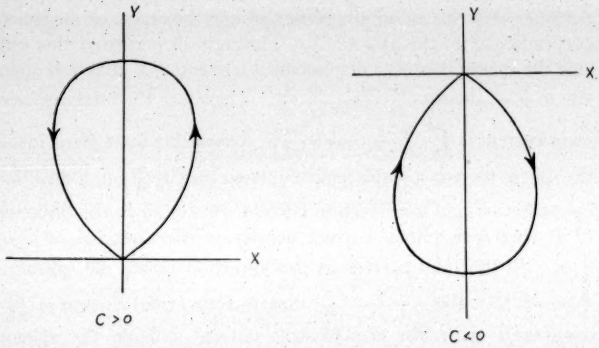
1. A charge e has a velocity v along the axis of X. The curves for the displacement current—with reference to axes moving with the charge—are the same as those of the displacement due to a doublet of strength ev, with its axis along the axis of X.

The direct proof is as follows:

$$\varphi = \frac{e}{\varepsilon r};\quad E_x = -\frac{\partial \varphi}{\partial x} = \frac{ex}{\varepsilon r^3};\quad E_y = \frac{ey}{\varepsilon r^3}$$

$$i_x = -\frac{\varepsilon v}{4\pi}\frac{\partial E_x}{\partial x} = \frac{ve}{4\pi}\frac{2x^2 - y^2}{r^5};\quad i_y = \frac{ve}{4\pi}\frac{3xy}{r^5}$$

FIG. 1.



Hence the differential equation of the curves is

$$\frac{dy}{dx} = \frac{3xy}{2x^2 - y^2}$$

the solution of which is $(x^2 + y^2)^{3/2} = Cy^2$ or, in polar coördinates $r = C \sin^2 \vartheta$, *i.e.*, the well-known equation for the lines of displacement due to a doublet.

Typical curves for $C > 0$ and $C < 0$ are shown in Fig. 1. Each "tube" of displacement current has an infinitesimal gap at the origin which is closed by the *convection* current due to the moving charge; so that the vector $\frac{\partial D}{\partial t} + \rho \bar{v}$ is solenoidal.

This solenoidal condition may be explained more in detail. Let the moving charge e be distributed uniformly through a sphere of radius R, so that $e = \frac{4}{3}\pi R^3 \rho$. For points *outside* the sphere

the tubes of displacement current are the same as those of displacement due to a doublet of strength $e\bar{v}$ placed at the centre, *i.e.*, $i_x = \frac{ev}{4\pi}\frac{2x^2-y^2}{r^5}$, $i_y = \frac{ev}{4\pi}\frac{3xy}{r^5}$. For points *inside* the sphere $E_x = \frac{4}{3}\frac{\pi\rho x}{\varepsilon}$, $E_y = \frac{4}{3}\frac{\pi\rho y}{\varepsilon}$ and therefore $i_x = -v\frac{\varepsilon}{4\pi}\frac{\partial E_x}{\partial x} = -\frac{v}{3}\rho$ and $i_y = 0$. In addition, there is a convection current inside of density ρv in the direction of the X axis. At the surface the normal component of the current density outside is $i_x \cos\vartheta + i_y \sin\vartheta = \frac{evx}{2\pi R^4}$, and inside it is $\frac{3}{2}v\rho\cos\vartheta = \frac{evx}{2\pi R^4}$.

If one wishes to consider total currents, rather than current densities, describe an infinite plane through the centre of the sphere perpendicular to the axis of X. Through all points of this outside the sphere there is a displacement current, in a direction opposite to $\bar{v}$, of density $\frac{ev}{4\pi}\frac{y^2}{r^5} = \frac{ev}{4\pi}\frac{1}{r^3}$. Therefore the total displacement current is $\int_R^\infty \frac{ev}{4\pi}\frac{1}{r^3}2\pi r\,dr = \frac{ev}{2R}$. Across this same plane inside the sphere there is a displacement current density $\frac{v}{3}\rho$ in a direction opposite to $\bar{v}$ and a convection current density ρv in the direction of $\bar{v}$, therefore a total current density in the direction of $\bar{v}$ of $\frac{2}{3}\rho v$. So the total current in this direction inside the sphere is $\frac{2}{3}\rho v.\ \pi R^2$. But $\rho = \frac{3}{4}\frac{e}{\pi R^3}$; therefore this total current is $\frac{ev}{2R}$, continuous with the displacement current outside the sphere. All of what has just been proved holds equally well if the dielectric of the sphere through which the charge is uniformly distributed is different from the dielectric outside.

It may not be without interest to note that even in this latter case the electromagnetic force on the sphere produced when the charge is moving through a uniform magnetic field is due to the convection current only. According to Ampère's law, the force acting on an element ds of conduction current J when placed in a magnetic field of intensity H is $\mu\frac{J}{c}[\bar{ds}.\bar{H}]$. In the case of the moving sphere, let the magnetic field be at right angles to the line of motion. The total convection current through an element of an equatorial plane perpendicular to the line of motion is $\rho v.\ 2\pi\ y\ dy$; its length inside the sphere is $2x$; therefore the force on the whole

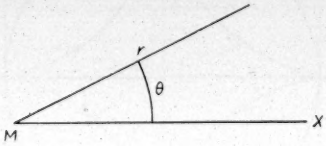
sphere is $\frac{\mu}{c} H \int_0^R \rho v.\ 2\pi\ y.\ 2x.\ dy = \frac{\mu}{c} \frac{4}{3} \pi \rho R^3\ v\ H = \frac{\mu}{c}\ e\ v\ H$, the well-known value. Consequently, the displacement current inside the sphere, of density $-\frac{1}{3}\rho v$, as appears to a stationary observer, does not contribute to this force.

2. A doublet of strength M has a velocity $\bar{v}$ in the direction of its axis. This is again a case of axial symmetry.

The curves for the displacement current are the same as those of the displacement for the combination of a doublet of strength $\frac{M}{\alpha}$ and one of strength $-\frac{M}{\alpha}$ displaced in the opposite direction to $\bar{v}$ by an amount αv.

The direct proof is as follows (Fig. 2):

FIG. 2.



$$\varphi = \frac{M \cos \vartheta}{\mathfrak{S} r^2} = \frac{Mx}{\mathfrak{S} r^3}$$

$$E_x = -\frac{\partial \varphi}{\partial x} = \frac{3\,Mx^2}{\mathfrak{S} r^5} - \frac{M}{\mathfrak{S} r^3};\quad E_y = \frac{3Mxy}{\mathfrak{S} r^5}$$

$$i_x = -v \frac{\mathfrak{S}}{4\pi} \frac{\partial E_x}{\partial x} = \frac{v}{4\pi} \left(\frac{15Mx^3}{r^7} - \frac{9Mx}{r^5} \right);$$

$$i_y = -\frac{v\mathfrak{S}}{4\pi} \frac{\partial E_y}{\partial x} = \frac{v}{4\pi} \left(\frac{15Mx^2y}{r^7} - \frac{3My}{r^5} \right)$$

$$i_x = \frac{v}{4\pi} \frac{3Mx}{r^7} (2x^2 - 3y^2);\quad i_y = \frac{v}{4\pi} \frac{3My}{r^7} (4x^2 - y^2).$$

Hence the differential equation of the curves for the displacement current is $\frac{dy}{dx} = \frac{y}{x} \frac{4x^2 - y^2}{2x^2 - 3y^2}$; the solution of which is $(x^2 + y^2)^{5/2} = C\,xy^2$; or, expressed in polar coördinates, $r^2 = C.\cos\vartheta \sin^2\vartheta$. This is the well-known equation for the combination of doublets referred to previously.

Typical curves for $C > 0$ and $C < 0$ are shown in Fig. 3.

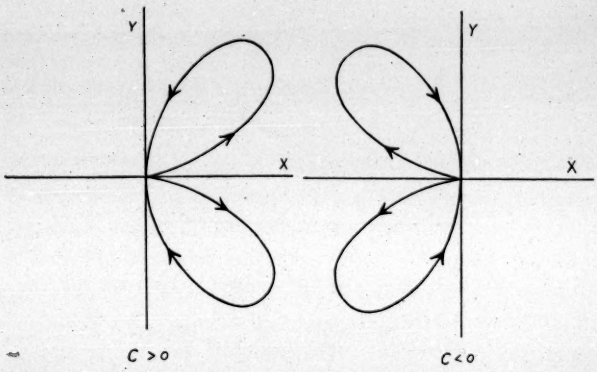
For $C = \infty$, $x = 0$ and $y = 0$.

At all points along the lines $2x = \pm y$, the curves are parallel to the X axis, etc.

At the origin each curve has an infinitesimal "gap" which is closed by the convection current due to the moving doublet. All the curves for $C > 0$ are closed by the convection current due to the moving plus charge of the doublet, while the curves for $C < 0$ are closed by the motion of the negative charge.

This solenoidal condition may be described more in detail. Let the doublet be considered as a polarized sphere of radius R,

FIG. 3.



the strength M being equal to eh. The following quantities must be calculated:

(a) Displacement current density, in dielectric immediately outside the sphere. From what has just been proved

$$i_{x_1} = \frac{3Mv}{4\pi R^5}\, x(2x^2 - 3y^2); \quad i_{y_1} = \frac{3Mv}{4\pi R^7}\, y(4x^2 - y^2)$$

(b) Displacement current density in the surface layer of the sphere. A simple calculation gives for this

$$i_{x_2} = -\frac{3ev}{4\pi R^5}\, x^2 + \frac{3Mvx}{4\pi R^7}\,(2x^2 - 3y^2); \quad i_{y_2} = -\frac{3ev}{4\pi R^5}\, xy + \frac{3Mv}{4\pi R^7}\, y\,(4x^2 - y^2)$$

(c) Convection current density in surface layer

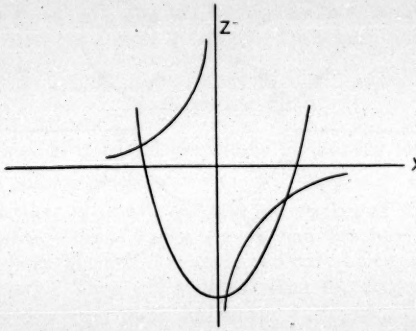
$$i_{x_3} = \rho v = \frac{3ev}{4\pi R^3}; \quad i_{y_3} = 0$$

N. B.—In the spherical space enclosed by the surface layer, E is uniform; hence $\frac{\partial \bar{D}}{\partial t} = 0$.

It is seen that i_{x_2} and i_{y_2} are made up of two terms; the second ones are identical with i_{x_1} and i_{y_1}; and the first ones are components of a vector $-\frac{3ev}{4\pi R^3}\frac{x}{R}$, normal to the surface, which is equal and opposite to the normal component of i_{x_3}. Consequently the normal component of the vector $\frac{\partial \bar{D}}{\partial t} + \rho\bar{v}$ is continuous through the surface.

The mechanism then of the total current is as follows: Outside

FIG. 4.



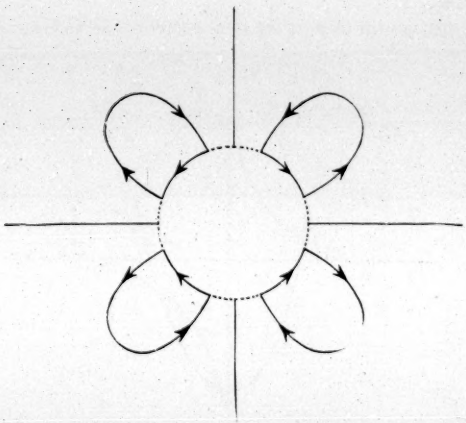
the sphere there is a flux of current away from the part of the surface near the axis, which returns again to the "polar" part of the surface; this current is continuous with and supplied by that part of the displacement current inside the surface layer due to the second terms in i_{x_2} and i_{y_2}; this current in turn is supplied by the tangential component of the convection current in the surface layer. Or, considered more simply, each tube of displacement current outside the sphere carries away a certain current from the surface where it starts and returns it to the surface where it ends, and this current is carried back to its starting point by the convection current in the surface.

The total flux of current may be calculated. The current density immediately outside the sphere has the components

$$i_x = \frac{3Mv}{4\pi R^7} x(2x^2 - 3y^2); \quad i_y = \frac{3Mv}{4\pi R^7} y(4x^2 - y^2)$$

and therefore the radial component $i_r = \frac{3Mv}{4\pi R^6}(2x^2 - y^2) = \frac{3Mv}{4\pi R^4}(3\cos^2\vartheta - 1)$. This component vanishes when $3\cos^2\vartheta - 1 = 0$, *i.e.*, when $\vartheta = \cos^{-1}\sqrt{\frac{1}{3}}$. This critical angle, which may be

FIG. 5.



called ϑ_0, denotes a certain point on the sphere such that for values of $\vartheta < \vartheta_0$ there is a current flux away from the sphere, and for values of $\vartheta > \vartheta_0$ the flux is returning to the sphere. The total flux away from the "axial cap" of the sphere is therefore

$$\int_0^{\vartheta_0} \frac{3Mv}{4\pi R^4}(3\cos^2\vartheta - 1) \cdot 2\pi R^2 \sin\vartheta \, d\vartheta = \frac{Mv}{R^2}\cos\vartheta_0$$

and there is, of course, an equal flux back to the sphere. (The same conditions prevail at the opposite axial cap of the sphere.)

The tangential component of the convection current density in the surface layer is $\rho v \sin\vartheta = \frac{3cv}{4\pi R^3}\sin\vartheta$ and is directed towards the axis. It flows through a surface, perpendicular to the tangent,

of area $h \cos \vartheta . 2\pi R \sin \vartheta$; therefore the current flux is $\frac{3eh}{2R^2} v \cos \vartheta \sin^2 \vartheta$. But $eh = \overline{M}$, and hence this flux at any angle ϑ is $\frac{3Mv}{2} \cos \vartheta \sin^2 \vartheta$. Its maximum value is for $\cos^2 \vartheta = \frac{1}{3}$, *i.e.*, at ϑ_0, because at this angle the current is the sum of all the partial currents, each of which joins the two open ends of a tube of current flowing outside the sphere. The total convection current, corresponding to the total flux of displacement current away from the sphere and back to it, is found by making $\vartheta = \vartheta_0$; this is $\frac{Mv}{R^2} \cos \vartheta_0$. This is simply a consequence of the proof previously given that the vector $\frac{\partial \overline{D}}{\partial t} + \rho \overline{v}$ is solenoidal.

It may be of interest to investigate the intersections of any one curve $r^5 = C\, xy^2$, *e.g.*, one for which $C > 0$, with a circle of radius R described around the origin. On substitution, the equation for x is

$$x^3 - xR^2 = -\frac{R^5}{C}$$

This may be discussed graphically by drawing the hyperbola $xz = -\frac{R^5}{C}$ and the parabola $x^2 - z = R^2$. (Fig. 4.) It is seen at once that there is always one real intersection of these curves, for a positive value of z; but $y^2 = -z$, and therefore, although x is real, y is imaginary. The other two intersections may be real or imaginary. They will coincide when the original equation for x has two equal roots, *i.e.*, when $x^2 = \frac{R^2}{3}$, $x^3 = \frac{R^5}{2C}$, or when $R^2 = \frac{2}{3}\sqrt{\frac{1}{3}}\, C$. This gives the radius of the circle which circumscribes the original curve for a definite value of C. (The point of tangency of the circle and curve has, obviously, the coördinates $\sqrt{\frac{1}{3}}\, R$ and $\pm\sqrt{\frac{2}{3}}\, R$, or R and $\cos^2 \vartheta = \frac{1}{3}$.) For values of R less than this critical one, the lower branch of the hyperbola has two real intersections, for each of which z is negative and therefore y is real. For values of R greater than this critical value, the two intersections are imaginary, and therefore y is imaginary. Summary: The intersections of the circle of radius R with the curve $r^5 = C\, xy^2$ are given as follows in terms of the radius of the circumscribing circle R_0.

(1) $R < R_0$, x has 3 real roots, $\pm y$ has 2 real values, 1 of which is imaginary; therefore there are 4 points of intersection.

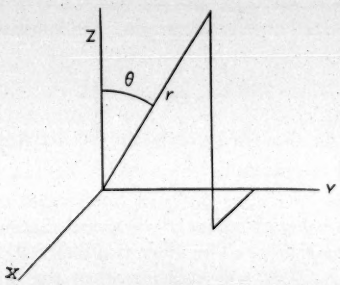
(2) $R = R_0$, x has 3 real roots, 2 of which coincide, etc.; condition of tangency.

(3) $R > R_0$, x has 1 real root and 2 imaginary ones; all values of y are imaginary; therefore there is no intersection in real points.

3. An uncharged dielectric or conducting sphere moves with a velocity $\overline{v}$ in and parallel to a uniform field of force.

When such a sphere of radius R is in a uniform field of force of intensity $\overline{E}$, the field at points outside the sphere is modified

FIG. 6.



by the addition of a field due to a doublet of strength $M = \alpha R^3 E$ placed at the centre of the sphere with its axis parallel to the field. (For a conductor $\alpha = 1$, for a dielectric $\alpha < 1$.) Inside the sphere the field is uniform or zero. When the sphere is moving, therefore, in the direction of the field, there is no change at a point inside the sphere, *i.e.*, there is no displacement current inside; and, for points outside the sphere, the displacement currents are simply those due to a moving doublet, as given in the previous illustration.

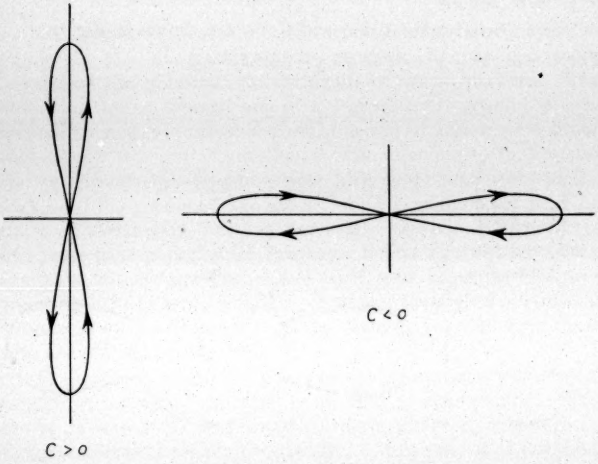
A typical set of curves is then as shown in Fig. 5. Each branch of each curve is closed by the current along the surface of the sphere, due to the component of the velocity tangent to the sphere of the apparent or real charge of surface density P_n or σ.

4. A doublet of strength M has a uniform velocity $\overline{v}$ at right angles to its axis.

In the previous cases there was axial symmetry, but not in this.

Choose the Z axis as that of the doublet, and the Y axis as that of the velocity. (Fig. 6.)

FIG. 7.



$$\varphi = \frac{M\cos\vartheta}{\varepsilon r^2} = \frac{Mz}{\varepsilon r^3}$$

$$E_x = \frac{3Mxz}{\varepsilon r^5};\quad E_y = \frac{3Myz}{\varepsilon r^5};\quad E_z = \frac{3Mz^2}{\varepsilon r^5} - \frac{M}{\varepsilon r^3}$$

$$-\frac{\partial E_x}{\partial y} = \frac{15Mxyz}{\varepsilon r^7};\quad -\frac{\partial E_y}{\partial y} = \frac{15My^2z}{\varepsilon r^7} - \frac{3Mz}{\varepsilon r^5};$$

$$-\frac{\partial E_z}{\partial y} = \frac{15Myz^2}{\varepsilon r^7} - \frac{3My}{\varepsilon r^5}$$

Hence the differential equation of the displacement current curves is given by

$$dx : dy : dz = 5\,xyz\,r^{-2} : z\,(5y^2r^{-2} - 1) : y\,(5z^2r^{-2} - 1)$$
$$= 5\,xyz : z\,(4y^2 - x^2 - z^2) : y\,(4z^2 - x^2 - y^2)$$

Therefore, in the $Y-Z$ plane, the equation of the curves is

$$\frac{dy}{dz} = \frac{z\,(4y^2 - z^2)}{y\,(4z^2 - y^2)}$$

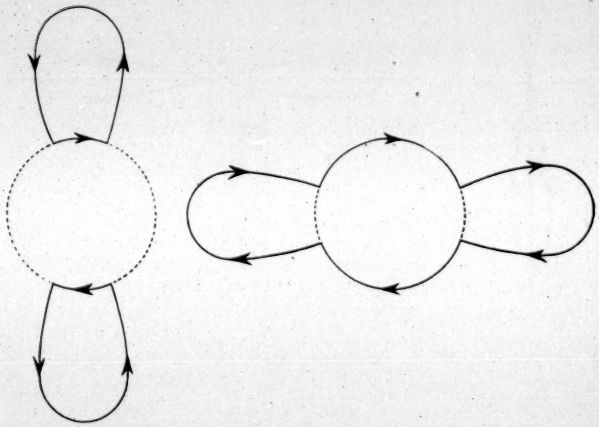
The solution of which is

$$(z^2 + y^2)^{5/3} = C\,(z^2 - y^2)$$

or $r^{4/3} = C.\ \cos 2\theta$.

Typical curves for $C > 0$ and $C < 0$ are shown in Fig. 7. For $C = \infty$, $z^2 - y^2 = 0$, or $z - y = 0$ and $z + y = 0$.

FIG. 8.



The continuity of the curves at the origin is maintained by the convection currents due to the motion of the positive and negative charges making up the doublet.

Considering the doublet as due to a sphere polarized in the direction of the Z axis, and drawing typical curves for $C > 0$ and $C < 0$ in the $Y-Z$ plane, together with the convection currents which makes these curves continuous, it is seen that they are as shown in Fig. 8.

THE ACOUSTICS OF ROOMS.

REVERBERATIONS.*

BY

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THE problem of architectural acoustics like those of traffic regulation and of transportation generally has become acute because of the industrial developments of recent decades. The increasing use of concrete and of fire-proof construction has confronted us with acoustical horrors, the like of which were probably unknown to our forefathers. The attempts to understand and to mitigate this situation were little more than stabs in the dark until the genius of Professor Sabine brought order into the chaos of speculation that had previously existed. Some twenty odd years have passed since Professor Sabine's results have been available and even to-day rooms with poor acoustical features are being built in large numbers. Some of these receive remedial treatment; others remain a continual source of irritation to those who are obliged to use them.

The question arises whether reasonably satisfactory acoustical conditions can now be assured in advance of construction. This can be answered in the affirmative. Some architects secure satisfactory acoustical results consistently. Then why is it not done more generally? Probably because many architects find it difficult to understand and to utilize the data which the researches of physicists have made available. A few physicists are assisting architects with their acoustical problems. More coöperation of this kind will help make each room acoustically satisfactory to the extent of our present knowledge. Further research will enable us to do much better in the future.

The most important difficulty encountered in public assembly rooms is that of reverberation. One of its annoying manifestations is the persistence of a sound in the room after the sound source has ceased to emit. Because of reverberation the sound heard at any moment by the individuals of an audience is due not

* Presented at the Stated Meeting of the Institute held Wednesday, January 17, 1923.

to a single syllable uttered by the speaker, but to a number of consecutive syllables, and this necessarily leads to confusion.

In order to know how this confusion may be eliminated, it is necessary to determine just how it arises.

If somewhere in a closed room we begin to emit sound at a constant rate, the nearest surface will be the first to reflect, and an appreciable time will elapse before the remotest surface participates in the reflection, this time being longer the larger the room. For every quantity of sound energy E incident on the walls a definite fraction a is absorbed on the average. With advancing time the quantity of sound energy which falls upon the surfaces of the room will increase and consequently the rate of absorption by the walls will grow until it equals the rate of emission by the source. When this condition is reached the average sound intensity in the room has a maximum value, which will be maintained as long as the sound emission continues unchanged.

If now the sound emission is stopped, the sound intensity will gradually diminish until all the energy has been absorbed by the surfaces of the room. The rate of absorption is always proportional to the amount of energy present and the sound intensity therefore falls off at a progressively decreasing rate.

But a qualitative consideration of the situation, while helpful, is not sufficient for practical purposes. We shall find it profitable to derive formulas, describing the growth and decay of sound intensity in a room and to use them in our further consideration of the reverberation problem. Such formulas have been developed by Jaeger.[1] A hitherto unpublished derivation of these equations by Buckingham has several advantages which commend it for our use. Buckingham considers the sound energy divided up into a very large number of equal parts and assumes that in the steady state, when the sound intensity is stationary, these energy units are uniformly distributed throughout the room, both with respect to position and to direction of motion. These assumptions, which are the same as those made by Jaeger, ignore the existence of interferences and the equations which follow are valid only to the extent to which interference phenomena may be ignored. All the energy units are of course moving with a constant speed, that of sound.

[1] Jaeger, G., "Zur Theorie des Nachhalls," *Wiener Sitzungsberichte*, 120, May, 1911.

We shall consider an element of volume dV anywhere in the room and an element of surface ds also chosen at random. The distance from the centre of the volume element to the centre of the surface element we shall denote by r. If N is the number of energy units per unit volume, the volume dV will contain NdV such units. If $d\omega$ is the solid angle subtended at the volume element by ds the number of energy units in dV which are moving in direction which pass through ds is $NdVd\omega/4\pi$. If θ is the angle between the normal to the surface element ds and the direction r we may write $d\omega = ds\cos\theta/r^2$. The number of energy units in dV which will ultimately pass through ds is, therefore, given by

$$\frac{NdVds\cos\theta}{4\pi r^2} \tag{1}$$

If dV is taken to include the space between r and $r + dr$ and θ and $\theta + d\theta$, we may write

$$dV = 2\pi r\sin\theta \cdot rd\theta dr$$

and substituting in (1), the number of energy units which at any moment are contained in dV and which will ultimately reach ds is given by

$$\frac{1}{2} Ndsdr\sin\theta\cos\theta d\theta \tag{2}$$

For the whole hemispherical shell between r and $r + dr$ this is

$$\frac{1}{2} Ndsdr\int_0^{\pi/2}\sin\theta\,\mathrm{ccs}\,\theta d\theta = \frac{1}{4} Ndsdr \tag{3}$$

If we integrate with respect to r from $r = 0$ to $r = v$ = the velocity of sound, *i.e.*, over a hemisphere of radius v about ds as centre, we get the whole number of energy units that are moving toward the surface element ds and are near enough to reach it in one second.

The number of energy units reaching any bounding surface ds per unit time is, therefore,

$$\frac{1}{4} Nds\int_0^v dr = \frac{1}{4} Nvds \tag{4}$$

or if E = energy per unit volume, the energy incident upon any

finite surface area S per unit time is given by $\frac{1}{4} EvS$ and that absorbed per unit time, by

$$a \frac{1}{4} EvS \tag{5}$$

where a = the coefficient of absorption peculiar to the area S. We may, therefore, at once write down the differential equation for the sound intensity in a closed room,

$$V \frac{\partial E}{\partial t} + \frac{1}{4} vaSE = A \tag{6}$$

where A = the rate of sound energy emission, assumed constant.

We shall find the solutions of equation (6) for the following special cases useful.

A. Uniform sound emission beginning at zero time. The solution for this case is

$$E = \frac{4A}{vaS}\left[1 - \varepsilon^{-\frac{vaS}{4V}t}\right] \tag{7}$$

B. The steady state has been reached by uniform sound emission.

In this case $\frac{\partial E}{\partial t} = 0$ and $E = E_{max.}$ Hence

$$E_{max} = \frac{4A}{vaS} \tag{8}$$

C. Emission stopped after the steady state has been reached. Then $A = 0$ and the solution for this case is

$$E = \frac{4A}{vaS} \varepsilon^{-\frac{vaS}{4V}t} \tag{9}$$

or

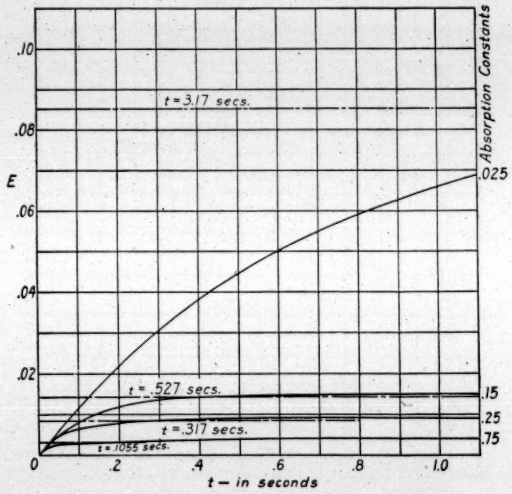
$$E = E_{max} \varepsilon^{-\frac{vaS}{4V}t} \tag{10}$$

Equation (7) describes the growth of sound intensity in a room when sound is being emitted at a constant rate. The maximum intensity reached is given by equation (8). As far as properties of the room are concerned the maximum intensity is determined by the product $a.S$. This quantity was called by Sabine the absorbing power of the room. We conclude from equations (7) and (8) that the larger the absorbing power of the room the less intense will be the sound of a voice or a musical instrument. The volume of the room determines the intensity

only to the extent to which it determines the magnitude of the area S. Any changes in volume which can be made without changing the size and character of its surface areas will have no effect upon the absorbing power and hence upon the intensity.

It follows at once from equation (8) that for a given rate of sound emission the maximum intensity attained decreases as the absorbing power of the surfaces increases. This is shown graphically in Fig. 1 for a room of 1000 cubic metres volume.

FIG. 1.



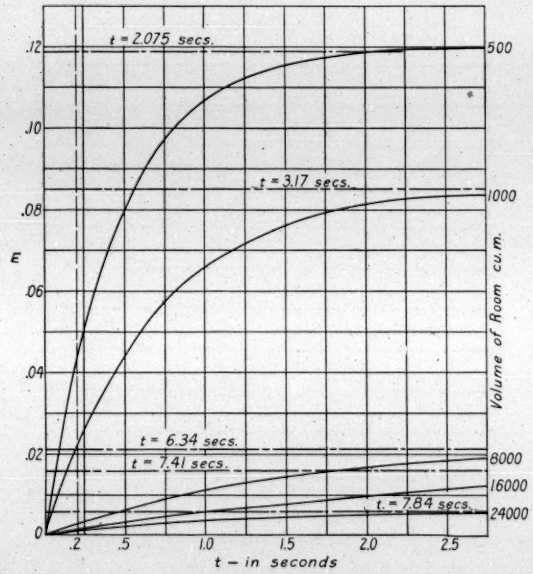
Growth of sound intensity in a room for various degrees of absorption of its boundaries. The time values associated with the horizontal dot and dash lines give the time in which the intensity grows to 99 per cent. of the saturation value.

These curves cover the range from practically the smallest to the largest absorption coefficients actually realizable. For a small absorption coefficient the intensity rises slowly toward a large maximum. For a large absorption coefficient the intensity rises rapidly toward a relatively much smaller maximum.

On the other hand, the rate at which the intensity approaches its maximum is determined by the ratio aS/V. The maximum is reached the more quickly the larger this quantity. We shall see

later that this ratio has a preferred value.[2] In going to larger rooms the value of $\frac{S}{V}$ necessarily decreases. In order to retain the preferred value of the ratio in this case a must be increased in the ratio that $\frac{S}{V}$ decreases. In other words, with increasing size the absorption per unit area of rooms must be increased in

FIG. 2.



Growth of sound intensity in rooms of different volumes, the boundaries being of the same poorly absorbing material in all cases.

order that satisfactory acoustical conditions may be assured. Failure to recognize this fact has led to a number of costly failures in the design of auditoriums.

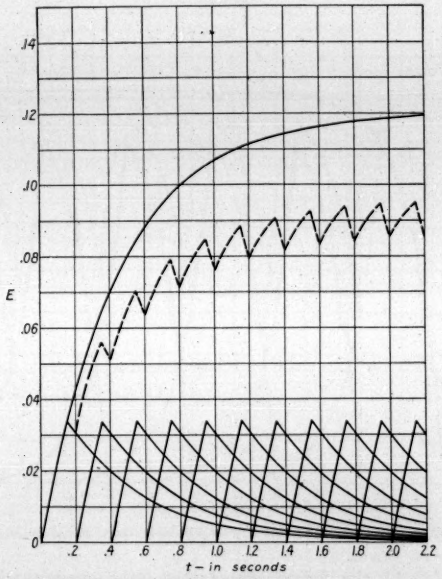
In Fig. 2 are shown the sound intensity-growth curves for rooms of different volumes. The absorption constants were assumed the same for all of them. The curves indicate that for

[2] The term optimum is avoided because the quantity has no mathematical maximum or minimum.

a given a the intensity rises more slowly the larger the room. The value of the rate of emission A in computing all the curves in this paper is that attributed to the average speaking voice.[3]

We shall now use the intensity-growth and decay equations in considering speech in a room, a case of discontinuous emission. In ordinary reading or speaking the average time interval per

FIG. 3.



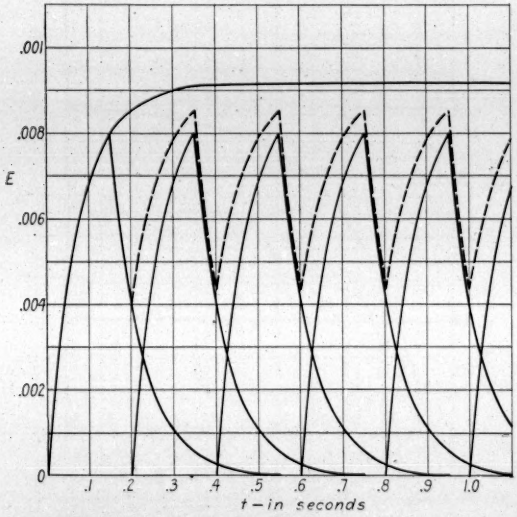
Growth and decay of sound intensity for syllable emission in a room of too small absorbing power.

syllable is not far from .2 second. The accuracy of this value will not affect our conclusions appreciably. We shall assume that for each syllable emission proceeds at a constant rate and that successive syllables are separated by intervals of .05 second during which no emission occurs. In Fig. 3 are shown the intensity-

[3] "Analysis of the Energy Distribution in Speech," I. B. Crandall and D. MacKenzie, *Phys. Rev.*, March, 1922, **19**, p. 221.

growth and decay curves of a number of successive syllables, computed for a room of small absorbing power. The total intensity-time curve for the room is obtained by adding the intensity-time curves of all the syllables. This is shown as the dash line curve in the figure. It shows a piling up of sound and relatively small intensity changes between syllables. This is sufficient explanation for the impossibility of hearing comfortably in the room. The

FIG. 4.



Growth and decay of sound intensity for syllable emission in a room of proper absorbing power.

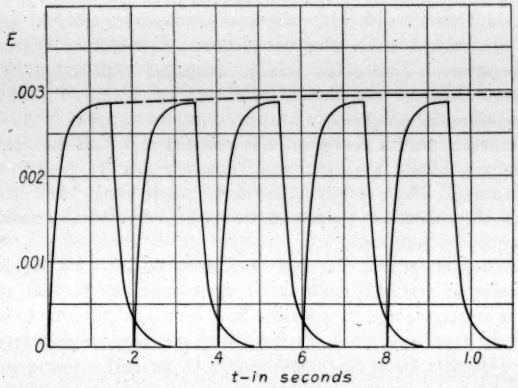
construction of the figure shows that improvement will result from a slower pace by the speaker, a fact which speakers would do well to keep in mind. The figure further indicates that although the slower pace may strike the speaker as being disjointed, the audience will receive no such impression. The upper curve in the figure shows the intensity which would obtain for perfectly continuous emission at the same rate.

Fig. 4 applies to a room of the same size as Fig. 3 in which, however, the interior finish has been so chosen as to provide satis-

factory acoustical conditions. The standards on which this choice is based will be discussed presently. In this room there is little of the piling up of sound energy and the intensity falls off considerably between syllables. It is rather obvious why this room should be more satisfactory than that to which Fig. 3 applies.

We may go several steps further and make the wall surfaces as absorbing as it is possible to do. The room to which Fig. 5

FIG. 5.



Growth and decay of sound intensity for syllable emission in a room of too great absorbing power.

applies is of this kind. It has the same volume as the rooms to which Figs. 3 and 4 apply. In this case the intensity for each syllable practically reaches the saturation value for continuous emission at the same rate. Very little sound intensity of a syllable remains when the succeeding syllable begins. The summation curve differs so little from the component curves that it has not been drawn.

The question is, "Why are the conditions of Fig. 5 not even better than those depicted in Fig. 4?" Anyone who has been in a felt-padded room knows that they are not. The answer is probably two-fold. First, the maximum intensity of speech in such a room is so very much below that obtaining in our usual surroundings that this circumstance impresses the observer as being

unnatural. The second point is that in our everyday surroundings we have become so accustomed to a certain amount of syllable overlapping that a departure from these conditions, even in the direction which *a priori* would seem to be more satisfactory, is regarded as unsatisfactory.

We see, therefore, that a room may have too little as well as too much reverberation. Too much reverberation results in confusion and too little is judged unsatisfactory for reasons not so evident. In the latter case the sound is described as being dead, lifeless. This at once raises the question whether general agreement can be had as to what constitutes a satisfactory degree of reverberation. This point was investigated experimentally by Professor Sabine,[4] who altered the absorbing powers of a number of rooms by the progressive introduction and removal of absorbing materials until a condition was reached at which the persons present considered a rendition of piano music to sound most satisfactory. These experiments were made most carefully to exclude all possibility of bias and the results revealed a remarkable uniformity of judgment.

Having recognized that there is a most satisfactory degree of reverberation and that substantial agreement can be had as to when it exists, we need to consider how we may determine to what extent the reverberation in a room which has been judged unsatisfactory departs from best conditions. If we had a sound intensity decay curve for a satisfactory room our problem of providing the best reverberation in all rooms would be simply that of bringing the intensity decay in each room into conformity with this optimum curve. But the decay curve, being logarithmic, is completely defined if we state in what interval of the variable t the quantity E decreases from the value $E_{max.}$ to $1/\varepsilon$ times that value. In conformity with the practice in similar physical problems this time interval may appropriately be called the relaxation time of the room and is given by

$$T_\varepsilon = \frac{4V}{va\bar{S}} \qquad (11)$$

This is the time in which the sound in a room decays from the saturation value to $1/\varepsilon$ times that value. The magnitude of this quantity T_ε, even for very large rooms, is a fraction of a

[4] Wallace C. Sabine, "Collected Papers on Acoustics," p. 71.

second. The impracticability of measuring or estimating sound intensity decay over so short a time interval makes the relaxation time thus defined unsuited for practical use. It would seem feasible to devise apparatus for recording the decay of sound intensity in a room with respect to time and to determine the value of T_ε from the graphical record. This was attempted by Professor Sabine and others, and it was found that the actual sound decay curve, instead of being nicely logarithmic, is in general a curve with many maxima and minima from which it is difficult to sift out the logarithmic component with sufficient precision. The complication of the curve is of course due to the interferences which we decided to ignore.

It is a remarkable fact that although the interferences close the avenue of approach just discussed, Professor Sabine succeeded in devising a workable procedure in spite of them. This he did by using as his starting point the minimum quantity of sound energy that is audible and by using 1,000,000 times this minimum quantity as the saturation energy density (sound intensity) at which the intensity decay begins. The time in which the decay from one value to the other takes place he called the reverberation time. This is expressed in terms of equation (10) as follows:

$$10^{-6} = \varepsilon^{-\frac{vaS}{4V}T} \tag{12}$$

where T = the reverberation time. The solution of this equation is[5]

$$T = \left(\frac{4}{v}\log_e 10^6\right)\frac{V}{aS} = .160\,\frac{V}{aS} \tag{13}$$

which is the reverberation time equation of Professor Sabine.

The decay of sound intensity in a room is, therefore, characterized by a measurable reverberation time. Since there is a best rate of intensity decay there is a best reverberation time. The amount of departure of the reverberation time from this best value is a measure of the departure of the reverberation from its most satisfactory degree.

[5] Since the velocity of sound enters into the constant of this equation, the constant varies with temperature. The value in equation (13) is based on a temperature of 20° C. or 68° F. If foot units are more convenient the reverberation time equation in terms of cubic feet volume and square feet area units is

$$T = .048\,\frac{V}{aS}$$

As presented here, the value of the constant in the reverberation time equation (13) results from the mathematical analysis of the reverberation problem. On the other hand, Professor Sabine derived the constant from actual reverberation experiments. The agreement of the theoretical and experimental values is remarkably good.

We can readily see by inspection of equation (13) how the reverberation time of a room may be computed in advance of construction.

We need to know only its volume and its absorbing power. The whole thing, therefore, practically dwindles down to computing the absorbing power of the room. In doing so we group all areas having the same absorption coefficient and multiply each such area by the absorption coefficient peculiar to it. The sum of the resulting products for all the component surfaces of the room is the absorbing power. Symbolically

$$\text{Absorbing power} = a_1S_1 + a_2S_2 + \cdots + a_nS_n = \sum_{i=1}^{i=n} a_iS_i \qquad (14)$$

The mean absorption coefficient used in the general formulas (7) to (9) is defined by the relation

$$a = \frac{\sum_{i=1}^{i=n} a_iS_i}{\sum_{i=1}^{i=n} S_i} \qquad (15)$$

After the absorbing power has been found by use of equation (14), substitution in (13) will yield the corresponding reverberation time.

Equation (14) is implicitly based on the assumption that the arrangement of the absorbing surfaces has no effect upon the magnitude of the absorbing power of the room and is valid only to the extent to which this assumption is in accord with the facts. In most cases encountered by the architect this accord is sufficiently good for practical purposes.

It is true, in general, that for satisfactory results the reverberation time should be a little greater than one second if the room is to be used for speaking, and a little less than two seconds if the room is to be used primarily for music. If mixed uses are contemplated a compromise must, of course, be made. If the com-

puted reverberation time departs from the optimum value, equation (13) may be used to determine how much change must be made in the absorbing power of the room to assure optimum conditions. If the reverberation time is too small some surface area must be made less absorbing by using material of smaller absorption coefficients. This can practically always be accomplished in a variety of ways and one can usually find at least one which is entirely compatible with other requirements. If, as is more usual, the reverberation time is too large, more absorbing materials must be provided in the construction. The quantity of absorbing power to be added usually gives a clue as to the best manner of securing it. In some cases none of the usual building materials will be adequate and material will have to be used for the sake of its sound-absorbing qualities alone. The most highly absorbing material known is hair felt, but it adds neither finish nor strength to the room in which it is used. The situation would be ideal if sound-absorbing materials were good finishing materials as well, so that interior finish and proper reverberation could be secured by the use of a single material. Development of building materials of this type is a problem of the future.[6] In order to have real practical utility such materials must be readily available and not prohibitively expensive.

It must not be forgotten that the people present in an auditorium contribute, usually appreciably and often preponderatingly, to the absorbing power of a room. It is therefore necessary when computing the reverberation time to be expected to include in the absorbing power of the room an item for the average estimated audience. The absorbing power per individual in an audience is given by Sabine[7] as .44 square metre unit.[8] For an estimated average audience of n people an absorbing power of .44 n must be added to the other component absorbing powers in computing the total for the room. If the audience is smaller than the estimated average the reverberation time will exceed the optimum

[6] An interesting example of a material of this type is the Guastavino tile.

[7] Sabine, "Collected Papers on Acoustics," p. 58.

[8] It must be remembered that this quantity .44 per individual is an *absorbing power* with the dimensions of an area. An average person absorbs as much sound energy as .44 square metre of a hypothetical totally absorbing substance (open window). If English units are used this number must be multiplied by 10.8, the number of square feet in a square metre.

value. An auditorium which is satisfactory with a capacity audience is, therefore, likely to be very unsatisfactory when most of the seats are unoccupied. On the other hand, an auditorium which would be satisfactory with 5 per cent. of a capacity audience would be dead with a full house. This difficulty can be minimized by designing the room acoustically for a capacity audience and by curtaining off unused galleries and alcoves for smaller audiences, thus simultaneously diminishing the volume and introducing highly absorbing surfaces.

It is quite impossible to discuss within the limits of this paper more than the merest fundamentals of the reverberation computations which can profitably be made in the course of design. We have thus far ignored the fact that the absorption coefficient of materials varies with the pitch of the sound and with its intensity. This is a difficulty but also a happy circumstance. Those who would provide reasonably good acoustics can usually overlook these facts. Those who would provide a masterpiece may not ignore them.

The procedure for correcting rooms which present unsatisfactory reverberation conditions is also indicated by the reverberation time equation (13). The reverberation time is determined experimentally in the vacant room and the volume is determined by measurement or from the plans. By substituting these values in the equation we obtain the magnitude of the absorbing power of the vacant room. From equation (13) we may also determine how much the absorbing power of the room should be in order to provide an optimum reverberation time. The difference of these two values is the corrective change of absorbing power which must be made. In most cases the absorbing power must be increased. In this case x, y, and z square feet of materials a, b, and c will give the desired amount of additional absorbing power. But there is not enough wall space available to apply x square feet of material a, and some surfaces are not suitable for treatment with material b. A combination of u square feet of material a and v square feet of material b gives the desired absorbing power and can be applied without harming the appearance of the room.

The whole procedure is relatively simple with the exception of the measurement of the reverberation time. It is not merely a matter of making a loud sound and measuring the duration of its audibility with a stop-watch. To be precise we must be certain

that the sound intensity in the room when the sound source is stopped off is 1,000,000 times the least audible intensity. If the initial sound were only 100,000 times the minimum audibility value the measured reverberation time would be too small by 16⅔ per cent. If we know the value of the initial intensity in terms of the minimum audibility intensity we can of course reduce the observed reverberation time to standard conditions. But the measurement of the initial intensity is quite difficult. The available devices for measuring sound intensity cannot be used effectively because the sound intensity at each point in the room is constantly changing due to the shifting interference pattern, and if the sound field were relatively stationary it would be necessary to make measurements at a large number of positions in order that the result might represent the average intensity throughout the room. Professor Sabine solved the problem of measuring the initial intensity elegantly by suitable reverberation time measurements.[9]

It is obvious that the correction of reverberation is not as simple as its avoidance. In most corrective problems coming within my personal experience the rooms investigated had only one-eighth to one-half of the optimum absorbing power. In such cases a value of the reverberation time which can be relied upon to be correct to 5, or even 10, per cent. may be of considerable value. We saw in equation (8) (p. 802) that the maximum intensity in the room is given by $4A/vaS$. The initial intensity in a room may, therefore, be computed from the rate of emission of the source and the absorbing power of the room. If we have a source of sound the rate of emission of which can be reliably reproduced, we can estimate the maximum intensity in a room to the same accuracy that we can estimate its absorbing power. If our estimate of the absorbing power ranges from five times too large to five times too small, the consequent error in the reverberation time will be less than 12 per cent. The reason for this is obvious from equation (13). With a little experience one can easily approximate the absorbing power well within these limits and relatively good reverberation times may be obtained.

The foregoing discussion is confined to only one phase of the acoustical problem confronting the architect. Reverberation is the most important of these problems and the one most frequently

[9] Sabine, "Collected Papers on Acoustics," pp. 34–40.

encountered. The focussing of sound by curved walls making the sound intensity abnormally large in some places and small in others is another difficulty to be considered. Loud echoes may result from this cause. Then there are resonances and interferences which defeat the aim to secure a uniform distribution of sound intensity.

We shall have to rest content, however, with our consideration of reverberation and I trust that its discussion here presented may be of some assistance to those interested in securing satisfactory hearing conditions in rooms.

Reciprocal Diffraction Relations between Circular and Elliptical Plates. JOHN COULSON and G. G. BECKNELL. (*Phys. Rev.*, Dec., 1922.)—"Early in the nineteenth century Poisson predicted that if the Huyghens-Fresnel theory were correct, the light intensity behind a small opaque disc illuminated by a point source should be about the same as though the disc were removed. Arago verified this experimentally, using a disc about 2 mm. in diameter. In a later paper Arago states that the same phenomenon was discovered by Delisle in 1715." In this series of experiments performed at the University of Pittsburgh a pinhole .3 mm. in diameter illuminated by an arc light served as the source of light, which fell upon a circular disc 2 metres distant. Five metres beyond the disc was placed the photographic plate on which the light impression was registered. This was merely a tiny circle of light when the disc was held perpendicular to the light from the pinhole. When the disc was turned about an axis in its plane the Arago spot developed into a figure with four cusps which expanded outward as the disc was turned further. The same figure was obtained by substituting for the turned disc an elliptical disc placed at right angles to the light, its minor axis equal to the diameter of the circular disc and its major axis determined according to the angle of rotation. "Careful measurements of the photographs prove that in each case the diffraction pattern is the evolute of the geometrical shadow. The effect is as though each element of the edge of the shadow contributed a spot along its normal, the result being a caustic curve of refraction." This consideration is pursued in a second paper in the same number of the *Review*. Further photographs were made with longer distances from the pinhole to the plate. In one case this distance was as much as 33 metres. Much information as to the structure of the diffraction figures was obtained. Very clear color effects were noted. This general conclusion is reached: "Any particular form of geometrical shadow is always associated with the same diffraction pattern whatever be the diffracting object." G. F. S.

THE SOLUTION OF DIFFERENTIAL EQUATIONS BY A METHOD SIMILAR TO HEAVISIDE'S.*

BY

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SYNOPSIS.

Systems of a Finite Number of Degrees of Freedom.—The classical method of solution of linear differential equations, together with the solution by means of Heaviside's expansion theorem, is briefly discussed. A new method, which is called for convenience "the method of elimination," of solving a linear differential equation of the second order with constant coefficients and a constant impressed force which is applied at the instant $t = 0$ is then given, and this is immediately extended to equations of the nth order. It is shown how the solution may be obtained when the equations have multiple roots, even though the method seems at first sight to break down. The application to the case of a force which can be represented by a Fourier series, and which is applied at the instant $t = 0$ follows. For the solution of this problem certain operators are derived by means of the method of successive approximations in integral equations.

Systems of an Infinite Number of Degrees of Freedom.—On solving certain of the partial differential equations in the flow of heat and electricity by the method of successive approximations in integral equations, a linear differential equation of an infinite order is obtained. By applying the "method of elimination" to this equation a solution is obtained which coincides with the one obtained by the classical theory. The points of resemblance of this solution to Heaviside's method of solution are noted and an operational notation very similar to his is adopted. An example is given which involves a partial differential equation of three independent variables. The possibility of the solution of potential problems is illustrated by some examples and the difficulties encountered are pointed out. A method of deriving definite integrals, by means of operators, is given, and a suggestion is made of the generalization of a result due to Fredholm.

* Communicated by E. J. Berg, D.Sc., Professor of Electrical Engineering.

INTRODUCTION.

The solution of certain problems in physics and engineering often resolves itself into the question of solving a system of linear differential equations with constant coefficients. Ordinarily the general solution of these equations is found and the constants of integration determined so as to fit the initial conditions. For example, it is known that the solution of the equation

$$\frac{d^n y}{dt^n} + a_1 \frac{d^{n-1} y}{dt^{n-1}} + a_2 \frac{d^{n-2} y}{dt^{n-2}} + \cdots + a_{n-1} \frac{dy}{dt} + a_n y = E \qquad (1)$$

is given by

$$y = \frac{E}{a_n} + A_1 e^{m_1 t} + A_2 e^{m_2 t} + \cdots + A_n e^{m_n t} \qquad (2)$$

where $m_1, m_2, \ldots m_n$ are the roots of the equation

$$m^n + a_1 m^{n-1} + a_2 m^{n-2} + \cdots + a_{n-1} m + a_n = 0 \qquad (3)$$

The method of solution of this problem seems to have been to make a guess at the form of the general solution and then to show that it satisfies the differential equation.

Heaviside introduced the symbol p for $\frac{d}{dt}$, subject to the condition that p^2 symbolized $\frac{d^2}{dt^2}$ and in general p^n symbolized $\frac{d^n}{dt^n}$, and he further assumed that p conformed (under certain restrictions) to the laws of ordinary algebra. Making this substitution equation (1) becomes

$$p^n y + a_1 p^{n-1} y + \cdots + a_{n-1} p y + a_n y = E \qquad (4)$$

Hence

$$y = \frac{E}{p^n + a_1 p^{n-1} + \cdots + a_{n-1} p + a_n} \qquad (5)$$

Splitting the expression on the right-hand side of this equation into partial fractions, it becomes,

$$y = \frac{c_1 E}{p - \alpha} + \frac{c_2 E}{p - \beta} + \cdots + \frac{c_n E}{p - \nu} \qquad (6)$$

where $\alpha, \beta, \ldots \nu$ are the roots of the polynomial in p in the

denominator of (5), and $c_1, c_2, \ldots c_n$ are constants which can easily be determined.

He then expanded each of these fractions in powers of $\frac{1}{p}$, and very ingeniously got a value for $\frac{1}{p-\alpha} = \frac{1}{-\alpha}(1 - e^{\alpha t})$ subject to the conditions that (a) the initial displacement of every coördinate shall be zero; (b) the initial velocity of every coördinate shall be zero. These two assumptions will be called Heaviside's terminal conditions.

From this he develops his "expansion theorem" [1] which is that, if $\frac{d}{dt}$ is replaced by p in the original equations and when these are solved in the usual manner, the symbolic equation

$$y = \frac{EY(p)}{Z(p)} \tag{7}$$

is obtained where $Y(p)$ and $Z(p)$ denote some functions of p, then the actual value of y under the conditions (a) and (b) is

$$y = E\left[\frac{Y(o)}{Z(o)} + \Sigma \frac{Y(p_m)e^{p_m t}}{p_m\left(\frac{dZ}{dp}\right)_{p=p_m}}\right] \tag{8}$$

where the summation is taken over the roots of $Z(p)$.

Heaviside's proof of this theorem, which is given in a footnote in his "Electrical Papers" (vol. 2, p. 373), has not seemed rigorous to mathematicians and in recent years other methods of proof have been evolved. Bromwich [2] gives a demonstration which depends upon the use of a certain contour integral, and Carson [3] solves it by going back to a consideration of the original differential equation.

The following method seems to have some advantage over both of these proofs, as it actually shows the mechanism through which the result is derived, and it allows the use of theorems concerning the convergence of infinite products in connection with the solution of a linear equation of an infinite order.

[1] Heaviside, "Electromagnetic Theory," vol. 2, p. 127 *et seq.* Also two papers by Cohen in recent numbers of this JOURNAL.

[2] Bromwich, *Proc. Lond. Mat. Soc.*, [Ser. 2] 1916, 15, p. 401.

[3] Carson, *Phys. Rev.*, N. S., 1917, 10, No. 3, p. 217.

SOLUTION OF LINEAR DIFFERENTIAL EQUATION OF SECOND ORDER.

Take as an example the simple equation

$$\frac{d^2y}{dt^2} + b\frac{dy}{dt} + c = E \tag{9}$$

where b, c, and E are constants. This can be written

$$\left(\frac{d}{dt} - \alpha\right)\left(\frac{d}{dt} - \beta\right) y = E \tag{10}$$

where α and β are the roots of the equation

$$m^2 + bm + c = 0.$$

Equation (10) is the usual operational way of writing (9), which will be found in most text-books on differential equations, and it is easily shown that the order of the operational factors may be reversed and the equation written

$$\left(\frac{d}{dt} - \beta\right)\left(\frac{d}{dt} - \alpha\right) y = E. \tag{10a}$$

Equation (10) can be solved by finding a function u such that

$$\left(\frac{d}{dt} - \alpha\right) u = E. \tag{11}$$

The solution of (11) subject to the condition $u = 0$ when $t = 0$ is

$$u = -\frac{E}{-\alpha}\left(1 - e^{\alpha t}\right) \tag{12}$$

Substituting this value of u in the left-hand side of equation (11) and equating to the left-hand side of (10) since both are equal to E, then

$$\left(\frac{d}{dt} - \alpha\right)\left[\frac{E}{-\alpha}(1 - e^{\alpha t})\right] = \left(\frac{d}{dt} - \alpha\right)\left(\frac{d}{dt} - \beta\right) y \tag{13}$$

which gives [4]

$$\frac{E}{-\alpha}\left(1 - e^{\alpha t}\right) = \left(\frac{d}{dt} - \beta\right) y \tag{14}$$

[4] Actually if

$$\left(\frac{d}{dt} - \alpha\right) A = \left(\frac{d}{dt} - \alpha\right) B$$

then

$$A - B = Ce^{\alpha t}$$

but for a solution subject to Heaviside's conditions $C = 0$.

Similarly find a function v such that subject to the condition $v = 0$ when $t = 0$

$$\left(\frac{d}{dt} - \beta\right) v = E \tag{15}$$

then

$$v = \frac{E}{-\beta}\left(1 - e^{\beta t}\right) \tag{16}$$

and proceeding in the same manner as above with (10a) instead of (10)

$$\frac{E}{-\beta}\left(1 - e^{\beta t}\right) = \left(\frac{d}{dt} - \alpha\right) y \tag{17}$$

subtracting (17) from (14) the $\frac{dy}{dt}$ term disappears and the result is

$$y = E\left[\frac{1}{\alpha\beta} + \frac{e^{\alpha t}}{\alpha(\alpha - \beta)} + \frac{e^{\beta t}}{\beta(\beta - \alpha)}\right]. \tag{18}$$

This is exactly the result which is obtained by applying Heaviside's expansion theorem. The important point to notice is that this equation of the second order is solved by means of the solution of two linear equations of the first order, and then by the elimination of $\frac{dy}{dt}$ from the resulting two equations.

SOLUTION OF SIMULTANEOUS EQUATIONS OF Nth ORDER.

The method of dealing with the general equation of the nth order is now apparent. If the above process is applied to each of the n factors $\frac{d}{dt} - \alpha_p$ where $p = 1, 2, 3, \ldots n$, the result is n equations in which the variables may be considered as $\frac{d^{n-1}y}{dt^{n-1}}$, $\frac{d^{n-2}y}{dt^{n-2}}$, $\ldots$ $\frac{dy}{dt}$, y, and provided the determinant of this system does not vanish, it is possible to determine y by elimination. If the equations are solved subject to Heaviside's terminal conditions his expansion theorem is obtained. If they are solved subject to arbitrary initial conditions, the n resulting constants can be determined so as to satisfy these conditions. For example (12)

is the solution of (11) only if $u = 0$ when $t = 0$. In general (12) could be written,

$$u = \frac{E}{-\alpha}\left(1 - C_1 e^{\alpha t}\right) \tag{12a}$$

Similarly (16) could be written

$$v = \frac{E}{-\beta}\left(1 - C_2 e^{\beta t}\right) \tag{16a}$$

and by elimination

$$y = E\left[\frac{1}{\alpha\beta} + \frac{C_1 e^{\alpha t}}{\alpha(\alpha-\beta)} + \frac{C_2 e^{\beta t}}{\beta(\beta-\alpha)}\right] \tag{18a}$$

where C_1 and C_2 are to be determined from the initial conditions. In the following the solution will be worked out subject to Heaviside's conditions, and it is evident the more general solution for an arbitrary initial state can be derived by multiplying each of the exponential terms in the result by arbitrary constants whose values are determined later in the usual way. The constant term, which corresponds to the permanent condition, is, however, independent of these arbitrary constants, as might be expected since the permanent condition does not depend upon the transient.

Let the system of linear differential equations be characterized by the following forms,

$$\begin{aligned}
a_{11}y_1 + a_{12}y_2 + \cdots\cdots + a_{1n}y_n &= F_1 \\
a_{21}y_1 + a_{22}y_2 + \cdots\cdots + a_{2n}y_n &= F_2 \\
\cdots\cdots\cdots\cdots\cdots\cdots & \\
\cdots\cdots\cdots\cdots\cdots\cdots & \\
a_{n1}y_1 + a_{n2}y_2 + \cdots\cdots + a_{nn}y_n &= F_n
\end{aligned} \tag{19}$$

the general coefficient a_{jk} being of the form

$$a_{jk} = \alpha_{jk}\frac{d^m}{dt^m} + \beta_{jk}\frac{d^{m-1}}{dt^{m-1}} + \cdots + \mu_{jk}$$

where α_{jk}, β_{jk}, . . . μ_{jk} are constants.

The impressed forces F_1, F_2, . . . F_n which begin to act at the time $t = 0$ will be assumed to be constants. It is most convenient to solve these equations for each impressed force one at a time, *i.e.*, assume first that F_1 acts and all the others are zero, then let F_2 act and all the others be zero, continuing this until the effect of each one of the forces has been found. The solution when all the forces act together is got by summing up the separate solutions.

The differential equation obtained for y_k from (19) when the force F_r is assumed to act alone is

$$Dy_k = M_{rk}F_r \tag{20}$$

where D is the value of the determinant,

$$\begin{vmatrix} a_{11} & a_{12} & \cdots\cdots & a_{1n} \\ a_{21} & a_{22} & \cdots\cdots & a_{2n} \\ \cdot\cdot & \cdot\cdot & & \cdot\cdot \\ \cdot\cdot & \cdot\cdot & & \cdot\cdot \\ \cdot\cdot & \cdot\cdot & & \cdot\cdot \\ \cdot\cdot & \cdot\cdot & & \cdot\cdot \\ a_{n1} & a_{n2} & \cdots\cdots & a_{nn} \end{vmatrix} \tag{20a}$$

and M_{rk} is the minor of the rth row and kth column.

Writing (20) out in full it becomes

$$\left(\frac{d}{dt}-\alpha\right)\left(\frac{d}{dt}-\beta\right)\cdots\cdot\left(\frac{d}{dt}-\nu\right)y_k = \left(\frac{d}{dt}-a_r\right)\left(\frac{d}{dt}-b_r\right) \cdots\cdot \left(\frac{d}{dt}-n_r\right)F_r \tag{21}$$

where $\alpha, \beta, \ldots \nu$ are the roots of D regarded as a function of $\frac{d}{dt}$ and $a_r, b_r, \ldots n_r$ are the roots of M_{rk}.

Determine ν functions $x_r^{(\alpha)}, x_r^{(\beta)} \cdots\cdot x_r^{(\nu)}$ such that subject to Heaviside's conditions,

$$\begin{aligned} \left(\frac{d}{dt}-\alpha\right)x_r^{(\alpha)} &= F_r \\ \left(\frac{d}{dt}-\beta\right)x_r^{(\beta)} &= F_r \\ \cdot\cdot \qquad & \qquad \cdot\cdot \\ \cdot\cdot \qquad & \qquad \cdot\cdot \\ \cdot\cdot \qquad & \qquad \cdot\cdot \\ \left(\frac{d}{dt}-\nu\right)x_r^{(\nu)} &= F_r. \end{aligned} \tag{22}$$

Then

$$\begin{aligned} x_r^{(\alpha)} &= \frac{F_r}{-\alpha}\left(1-e^{\alpha t}\right) \\ x_r^{(\beta)} &= \frac{F_r}{-\beta}\left(1-e^{\beta t}\right) \\ \cdot\cdot \qquad & \qquad \cdot\cdot \\ \cdot\cdot \qquad & \qquad \cdot\cdot \\ \cdot\cdot \qquad & \qquad \cdot\cdot \\ x_r^{(\nu)} &= \frac{F_r}{-\nu}\left(1-e^{\nu t}\right) \end{aligned} \tag{23}$$

Putting these values of $x_r^{(\alpha)}, x_r^{(\beta)} \cdots\cdot x_r^{(\nu)}$ in equations (22), then substituting the ν values of F_r so obtained in (21) and can-

celling out the common factor on both sides of the resulting equations, the following relations are obtained:

$$\left(\frac{d}{dt}-\beta\right)\left(\frac{d}{dt}-\gamma\right)\cdots\left(\frac{d}{dt}-\mu\right)\left(\frac{d}{dt}-\nu\right)y_k =$$
$$\left(\frac{d}{dt}-a_r\right)\left(\frac{d}{dt}-b_r\right)\cdots\left(\frac{d}{dt}-n_r\right)\frac{F_r}{(-\alpha)}\left(1-e^{\alpha t}\right),$$
$$\left(\frac{d}{dt}-\alpha\right)\left(\frac{d}{dt}-\gamma\right)\cdots\left(\frac{d}{dt}-\mu\right)\left(\frac{d}{dt}-\nu\right)y_k =$$
$$\left(\frac{d}{dt}-a_r\right)\left(\frac{d}{dt}-b_r\right)\cdots\left(\frac{d}{dt}-n_r\right)\frac{F_r}{(-\beta)}\left(1-e^{\beta t}\right)$$
$$\cdots\cdots\cdots

Subtracting the second equation in (25) from the first and dividing by $(\beta-\alpha)$.

$$\left(\frac{d}{dt}-\gamma\right)\left(\frac{d}{dt}-\delta\right)\cdots\left(\frac{d}{dt}-\nu\right)y_k$$
$$=F_r\left[\frac{(-a_r)(-b_r)\cdots(-n_r)}{(-\alpha)(-\beta)}+\frac{(\alpha-a_r)(\alpha-b_r)\cdots(\alpha-n_r)e^{\alpha t}}{\alpha(\alpha-\beta)}\right.$$
$$\left.+\frac{(\beta-a_r)(\beta-b_r)\cdots(\beta-n_r)e^{\beta t}}{\beta(\beta-\alpha)}\right] \tag{26}$$

Subtracting the third equation from the first and rearranging

$$\left(\frac{d}{dt}-\beta\right)\left(\frac{d}{dt}-\delta\right)\cdots\left(\frac{d}{dt}-\nu\right)y_k$$
$$=F_r\left[\frac{(-a_r)(-b_r)\cdots(-n_r)}{(-\alpha)(-\gamma)}+\frac{(\alpha-a_r)(\alpha-b_r)\cdots(\alpha-n_r)e^{\alpha t}}{\alpha(\alpha-\gamma)}\right.$$
$$\left.+\frac{(\gamma-\alpha_r)(\gamma-b_r)\cdots(\gamma-n_r)e^{\gamma t}}{\gamma(\gamma-\alpha)}\right] \tag{27}$$

By similarly subtracting the first and fourth, the first and fifth, etc., equations in (25) $(\nu-1)$ equations are derived.

Now subtract (27) from (26) and get after a slight simplification

$$\left(\frac{d}{dt}-\delta\right)\left(\frac{d}{dt}-\eta\right)\cdots\left(\frac{d}{dt}-\nu\right)y_k$$
$$=F_r\left[\frac{(-a_r)(-b_r)\cdots(-n_r)}{(-\alpha)(-\beta)(-\gamma)}+\frac{(\alpha-a_r)(\alpha-b_r)\cdots(\alpha-n_r)e^{\alpha t}}{\alpha(\alpha-\beta)(\alpha-\gamma)}\right.$$
$$\left.+\frac{(\beta-a_r)(\beta-b_r)\cdots(\beta-n_r)e^{\beta t}}{\beta(\beta-\alpha)(\beta-\gamma)}+\frac{(\gamma-a_r)(\gamma-b_r)\cdots(\gamma-n_r)e^{\gamma t}}{\gamma(\gamma-\alpha)(\gamma-\beta)}\right] \tag{28}$$

$(\nu-2)$ equations similar to (28) can be obtained. By continuing this process, which will be called the "method of elimination," the value of y_k is obtained in the standard form of Heaviside's expansion theorem. The general case may be easily proved by induction.

It might have been suggested perhaps that in equation (21) since F_r is a constant, the right-hand side could have been written $(-a_r)\ (-b_r)\ \ldots\ (-n_r)F_r$, and apparently if this had been done a different final expression for Heaviside's expansion theorem would have been obtained, *i.e.*, in (28) each of the numerators of the exponential terms would have been $(-a_r)\ (-b_r)\ \ldots\ (-n_r)$ instead of, for example, $(\alpha-a_r)(\alpha-b_r)\ \ldots\ (\alpha-n_r)$. This is due to the fact that F_r is a discontinuous function. It is zero when $t<0$ and equal to a constant value when $t>0$. The

method adopted above of performing the differential operations in (24), where the discontinuous function F_r has been replaced by the continuous functions $\frac{F_r}{-\alpha}(1 - e^{\alpha t})$, etc., avoids this difficulty.

CASE WHERE D HAS EQUAL ROOTS.

The method fails when D, regarded as a function of $\frac{d}{dt}$, has equal roots. Let α be a root of the nth order. Assume that these roots are not all equal but are $(\alpha + \varepsilon_1)$, $(\alpha + \varepsilon_2)$, . . . $(\alpha + \varepsilon_n)$ where $\varepsilon_1, \varepsilon_2, \ldots \varepsilon_n$ are small quantities which ultimately approach zero as a limit. Applying the method for the sake of brevity to the equation

$$\left(\frac{d}{dt} - \alpha\right)^n y = E \tag{29}$$

after these n equal roots have been replaced by the n unequal ones, the result is

$$y = \frac{E}{(-\alpha - \varepsilon_1)(-\alpha - \varepsilon_2)\cdots(-\alpha - \varepsilon_n)} + \frac{Ee^{(\alpha+\varepsilon_1)t}}{(\alpha + \varepsilon_1)(\varepsilon_1 - \varepsilon_2)(\varepsilon_1 - \varepsilon_3)\cdots(\varepsilon_1 - \varepsilon_n)} + \frac{Ee^{(\alpha+\varepsilon_2)t}}{(\alpha + \varepsilon_2)(\varepsilon_2 - \varepsilon_1)\cdots(\varepsilon_2 - \varepsilon_n)} + \cdots + \frac{Ee^{(\alpha+\varepsilon_n)t}}{(\alpha + \varepsilon_n)(\varepsilon_n - \varepsilon_1)\cdots(\varepsilon_n - \varepsilon_{n-1})} \tag{30}$$

The limit of the first term is evidently $\frac{E}{(-\alpha)^n}$. The other terms may be rewritten

$$Ee^{\alpha t}\left[\frac{1 + \varepsilon_1 t + \frac{\varepsilon_1^2 t^2}{2!} + \cdots}{(\alpha + \varepsilon_1)(\varepsilon_1 - \varepsilon_2)\cdots(\varepsilon_1 - \varepsilon_n)} + \frac{1 + \varepsilon_2 t + \frac{\varepsilon_2^2 t^2}{2!} + \cdots}{(\alpha + \varepsilon_2)(\varepsilon_2 - \varepsilon_1)\cdots(\varepsilon_2 - \varepsilon_n)} + \cdots + \frac{1 + \varepsilon_n t + \frac{\varepsilon_n^2 t^2}{2!} + \cdots}{(\alpha + \varepsilon_n)(\varepsilon_n - \varepsilon_1)\cdots(\varepsilon_n - \varepsilon_{n-1})}\right]$$

Picking out the coefficient of $\frac{t^q}{q!}$ inside this square bracket when $q < n$, it is seen to be the expansion in partial fractions of

$$\frac{(-1)^{n-1}\alpha^q}{(\alpha + \varepsilon_1)(\alpha + \varepsilon_2)\cdots(\alpha + \varepsilon_n)}$$

and the limit of this expression when $\varepsilon_1, \varepsilon_2, \cdots \varepsilon_n \longrightarrow 0$ is $\frac{(-1)^{n-1}}{\alpha^{n-q}}$

When $q \geqq n$ the coefficient is the expansion in partial fractions of

$$R = \frac{(-1)^{n-1}\alpha^q}{(\alpha+\varepsilon_1)(\alpha+\varepsilon_2)\cdots(\alpha+\varepsilon_n)} - (-1)^{n-1}\alpha^{q-n} - f(\alpha)$$

where $f(\alpha)$ tends to zero, when $\varepsilon_1, \varepsilon_2, \cdots \varepsilon_n \longrightarrow 0$. Hence when $\varepsilon_1, \varepsilon_2, \cdots \varepsilon_n \longrightarrow 0$, R itself tends to zero.

Thus the solution of (29) is

$$y = \frac{E}{(-\alpha)^n} + (-1)^{n-1}\frac{Ee^{\alpha t}}{\alpha^n}\left(1 + \alpha t + \frac{\alpha^2 t^2}{2!} + \cdots + \frac{\alpha^{n-1}t^{n-1}}{n-1!}\right) \quad (31)$$

This solution can be easily generalized to the case where $\alpha, \beta, \gamma, \ldots \nu$ are multiple roots of orders $m, n, p, \ldots s$, the multiple root α of order m giving rise to the exponential term

$$\frac{(-1)^{m-1}Ee^{\alpha t}}{\alpha^m(\alpha-\beta)^n(\alpha-\gamma)^p\cdots(\alpha-\nu)^s}\left[1 + \alpha t + \frac{\alpha^2 t^2}{2!} + \cdots\cdots \frac{\alpha^{m-1}t^{m-1}}{(m-1)!}\right]$$

with similar exponential terms for $\beta, \gamma, \ldots \nu$. The constant term is

$$\frac{E}{(-\alpha)^m(-\beta)^n\cdots(-\nu)^s}$$

APPLIED FORCE NOT A CONSTANT.

When the applied force can be represented by a Fourier series, if the solution can be found for each harmonic acting alone, then the sum of the solutions for each separate harmonic is the solution for the given applied force. The problem therefore resolves itself into finding a solution when the impressed force varies as a sine wave. There are several ways of proceeding in this case. Carson [5] gives a special expansion theorem, for which reference may be made to his paper. This method will not be discussed here. Heaviside replaces the impressed force $F \cos \omega t$ by the operator $\frac{p^2}{p^2+\omega^2}F$ and then applies his expansion theorem in the usual manner. The analogue of this method would be to notice that,

$$\left(1 + \omega^2 \int_0^t \int_0^t dt\, dt\right) F \cos \omega t = F \quad (32)$$

[5] Carson, *Phys. Rev.*, N. S., 1917, 10, No. 3, p. 217.

Hence operating on both sides of (21) with $\left(1+\omega^2\int_0^t\int_0^t dt\,dt\right)$ after having replaced F_r by $F_r \cos \omega t$ and changing the order of operations

$$\left(1+\omega^2\int_0^t\int_0^t dt\,dt\right)\left(\frac{d}{dt}-\alpha\right)\cdots\left(\frac{d}{dt}-\nu\right)y_k =$$
$$\left(\frac{d}{dt}-a_r\right)\left(\frac{d}{dt}-b_r\right)\cdots\left(\frac{d}{dt}-n_r\right)F_r \qquad (33)$$

where F_r is now a constant as before. Differentiating this twice, it becomes

$$\left(\frac{d^2}{dt^2}+\omega^2\right)\left(\frac{d}{dt}-\alpha\right)\left(\frac{d}{dt}-\beta\right)\cdots\left(\frac{d}{dt}-\nu\right)y_k =$$
$$\frac{d^2}{dt^2}\left(\frac{d}{dt}-a_r\right)\left(\frac{d}{dt}-b_r\right)\cdots\left(\frac{d}{dt}-n_r\right)F_r \qquad (34)$$

the solution of which is readily found by the Heaviside expansion theorem.

Similar operators can be found which transform $F \sin \omega t$, $Fe^{-\alpha t} \sin \omega t$, etc., into F and the expansion theorem thus extended to these cases. The determination of suitable operators will be briefly discussed in the next section.

Another mode of solution which is suggested by the method of elimination outlined above is to solve equation (22) where F_r is replaced by $F_r \sin \omega t$ or $F_r \cos \omega t$. This will give new values for $x_r^{(\alpha)}$, $x_r^{(\beta)}$, . . . $x_r^{(\nu)}$ in (23). Then substituting in (24) and using the method of elimination, the result is easily obtained. The final expression is not given here as it is rather cumbersome to write out in full.

SOLUTION OF INTEGRAL EQUATIONS BY SUCCESSIVE APPROXIMATIONS.

In order to apply the method outlined here to continuous systems, it will be necessary to use the method of successive approximations in the solution of integral equations.[6] To recall this method and at the same time derive some other results, a few examples will be taken.

Let

$$\left(\frac{d}{dt}-\alpha\right)y = E \qquad (35)$$

Integrating from o to t and rearranging

$$y = y_0 + Et + \alpha\int_0^t y\,dt \qquad (36)$$

[6] Whittaker and Watson, "Modern Analysis," 1915, 2nd ed., p. 215.

where $y_0 = (y)_{t=0}$. This is a linear equation of the second kind for y. The method of successive approximations is to substitute the value of y as given by the equation itself for y under the integral sign. Doing this and carrying out the integration on the first two terms, the equation becomes,

$$y = y_0 + y_0\alpha t + Et + E\alpha\frac{t^2}{2!} + \alpha^2\int_0^t\int_0^t y\,dt\,dt \tag{37}$$

Substituting again the value of y given by the equation under the integral sign and continuing the process, finally

$$y = y_0e^{\alpha t} + \frac{E}{-\alpha}(1 - e^{\alpha t}) \tag{38}$$

If Heaviside's terminal conditions apply, then $y_0 = 0$ and

$$y = \frac{E}{-\alpha}(1 - e^{\alpha t}) \tag{39}$$

In the case where $y_0 = 0$, equation (36) may be written

$$\left(1 - \alpha\int_0^t dt\right)y = Et \tag{40}$$

Differentiating this

$$\left(1 - \alpha\int_0^t dt\right)\frac{dy}{dt} = E \tag{41}$$

But from (39)

$$\frac{dy}{dt} = Ee^{\alpha t}. \tag{42}$$

Hence

$$\left(1 - \alpha\int_0^t dt\right)Ee^{\alpha t} = E \tag{43}$$

This equation shows that $(1 - \alpha\int_0^t dt)$ is the operator which transforms $Ee^{\alpha t}$ into the constant value E.

In a similar way, starting with the equation

$$\frac{d^2y}{dt^2} = -\omega^2y \tag{44}$$

and integrating twice from 0 to t

$$y = y_0 + y_1t - \omega^2\int_0^t\int_0^t y\,dt\,dt \tag{45}$$

where y_0 and y_1 are the values of y and $\frac{dy}{dt}$, respectively, when

$t = 0$. Solving this integral equation by successive approximations

$$y = y_0 \cos \omega t + \frac{y_1}{\omega} \sin \omega t \tag{46}$$

If $y_1 = 0$, substituting the value $y = y_0 \cos \omega t$ in (45), it can be written,

$$\left(1 + \omega^2 \int_0^t \int_0^t dt\, dt\right) y_0 \cos \omega t = y_0 \tag{47}$$

which is the operator already used in equation (32).

If $y_0 = 0$, then (45) can be written,

$$\left(1 + \omega^2 \int_0^t \int_0^t dt\, dt\right) \frac{y_1}{\omega} \sin \omega t = y_1 t \tag{48}$$

and on differentiating this

$$\frac{d}{dt}\left(1 + \omega^2 \int_0^t \int_0^t dt\, dt\right) \frac{y_1}{\omega} \sin \omega t = y_1 \tag{49}$$

Hence $\left(\frac{1}{\omega}\frac{d}{dt} + \omega \int_0^t dt\right)$ is the operator which transforms $y_1 \sin \omega t$ into the constant y_1.

Another result which will be required later in connection with problems on the cylinder is the solution of Bessel's equation of the nth order,

$$\frac{d^2y}{dt^2} + \frac{1}{t}\frac{dy}{dt} + \left(q^2 - \frac{n^2}{t^2}\right) y = 0 \tag{50}$$

If an attempt is made to integrate this equation directly, difficulties are encountered, since on the first integration the value of $\left(t \frac{dy}{dt}\right)$ when $t = 0$ is zero, and on the second integration the value of y when $t = 0$ is the constant term. Now since it is already known that $(y)_{t=0}$ or $J_n(qt)$ vanishes to the order t^n when $t = 0$, the integral equation, is really one of the first kind. The fact that $(y)_{t=0} = 0$ will become evident due to occurrence of infinite terms if the method of sucessive approximations is applied. Removing the factor t^n by the substitution $y = t^n z$ (50) becomes [7]

$$\frac{d^2z}{dt^2} + \frac{2n+1}{t}\frac{dz}{dt} + q^2 z = 0 \tag{51}$$

which may be written in the form

$$\frac{1}{t^{2n+1}} \frac{d}{dt}\left(t^{2n+1} \frac{dz}{dt}\right) + q^2 z = 0 \tag{52}$$

Integrating twice from 0 to t

$$z = z_0 - q^2 \int_0^t \frac{1}{t^{2n+1}} \int_0^t t^{2n+1} z\, dt\, dt \tag{53}$$

[7] Byerly, Fourier Series, p. 23.

where z_0 is the value of z when $t = 0$, it being taken that on the first integration the value of $t^{2n+1}\frac{dz}{dt}$ is zero when $t = 0$.

Equation (53) can be solved by successive approximations giving

$$z = z_0\left[1 - \frac{q^2t^2}{2(2n+2)} + \frac{q^4t^4}{2.4(2n+2)(2n+4)} - \text{etc.}\right] \qquad (54)$$

and since $y = t^n z$

$$y = z_0 t^n\left[1 - \frac{q^2t^2}{2(2n+2)} + \frac{q^4t^4}{2.4(2n+2)(2n+4)} - \text{etc.}\right] \qquad (55)$$

which is the standard form of $J_n(qt)$ when z_0 is suitably chosen. From (53) it is now evident that

$$\left(1 + q^2\int_0^t \frac{1}{t^{2n+1}}\int_0^t t^{2n+1}\,dt\,dt\right)\left(\frac{J_n(qt)}{t^n}\right) = 1 \qquad (56)$$

giving an operator which transforms $A\,\frac{J_n(qt)}{t^n}$ into the constant A.

A consideration of the lower limit in these integral equations brings out an interesting point. The complete specification of y at the time t would require that the lower limit of the integral, in (36) for instance, be taken as $-\infty$. Equations (37) and (38) are then equivalent to (36) only if $E = 0$ when $t < 0$; in other words, only if the force E is applied at the time $t = 0$. The same remarks apply to the other equations, and hence the operators derived above transform a force $Ee^{\alpha t}$, $E \sin \omega t$, etc., which is applied at the moment $t = 0$ into a constant force E applied at $t = 0$. Thus all these functions are discontinuous at $t = 0$, which is what is usually required in physical problems.

CONTINUOUS SYSTEMS.

Heaviside having derived his expansion theorem for an equation with a finite number of degrees of freedom, applies it to continuous systems and finds that it works. By its means he solved numerous partial differential equations, some of which have only been recently solved by other methods.[8] In the classical method a particular solution of the equation is first obtained and an infinite number of these added together so as to satisfy the initial conditions. In the recent book by Carslaw, "Introduction to the Mathematical Theory of the Conduction of Heat"

[8] *Cf.* Carslaw, "Conduction of Heat," 1921, p. 218, footnote; also p. 201.

(1922), some of the problems are worked out by four or five different methods, but in each of these solutions some initial assumption has to be made. It will now be shown how the application of the method of elimination enables the solution of a differential equation of an infinite order to be found and thus permits the solution of certain partial differential equations by a process which is purely mechanical. It will be found most convenient to take specific examples as illustrations. The first example is taken from Heaviside's work for the purpose of comparison. Most of the others will be found in the work by Carslaw referred to above, or in other works on heat. No attempt will be made here at a rigorous examination when infinite processes are involved.

TRANSMISSION LINE WITH RESISTANCE AND CAPACITY.

Consider a transmission line with resistance and capacity only. Let the line be short-circuited at the receiving end ($x = 0$) and let a constant voltage E be suddenly applied at the generating end ($x = l$) when $t = 0$.

The equations to be solved are

$$K \frac{\partial^2 v}{\partial x^2} = \frac{\partial v}{\partial t} \tag{57}$$

$$\left.\begin{aligned} &v = 0 \text{ when } x = 0 \\ &v = E \text{ when } x = l \quad (t > 0) \\ &v = 0 \text{ when } t = 0 \end{aligned}\right\} \tag{58}$$

where $K = \frac{1}{CR}$, C and R being the capacity and resistance of the cable per unit length. Integrating (57)

$$\frac{\partial v}{\partial x} = C_1 + \frac{1}{K}\int_0^x \frac{\partial v}{\partial t}\, dx \tag{59}$$

where $C_1 = \left(\frac{\partial v}{\partial x}\right)_{x=0}$ is a function of t only. On integrating again

$$v = C_1 x + \frac{1}{K}\int_0^x \int_0^x \frac{\partial v}{\partial t}\, dx\, dx \tag{60}$$

since $(v)_{t=0} = 0$ from (58). Solving this as an integral equation for v, remembering C_1 is a function of t alone, it becomes

$$v = \left(C_1 x + \frac{1}{K}\frac{\partial C_1}{\partial t}\frac{x^3}{3!} + \frac{1}{K^2}\frac{\partial^2 C_1}{\partial t^2}\frac{x^5}{5!} + \cdots \right) \tag{61}$$

This is a linear differential equation of infinite order for C_1. From (58) $v = E$ when $x = l$, hence writing C_1 outside the bracket for the sake of convenience

$$E = \left(l + \frac{1}{K}\frac{l^3}{3!}\frac{\partial}{\partial t} + \frac{1}{K^2}\frac{l^5}{5!}\frac{\partial^2}{\partial t^2} + \cdots\right) C_1 \tag{62}$$

But

$$\sinh p\theta = p\theta + \frac{p^3\theta^3}{3!} + \frac{p^5\theta^5}{5!} + \cdots \tag{63}$$

and also

$$\sinh p\theta = p\theta\left(1 + \frac{p^2\theta^2}{\pi^2}\right)\left(1 + \frac{p^2\theta^2}{2^2\pi^2}\right)\cdots\left(1 + \frac{p^2\theta^2}{n^2\pi^2}\right)\cdots \tag{64}$$

By comparing (63) and (64) it is evident (62) may be written in the factorial form

$$E = l\left(1 + \frac{\frac{l^2}{K}\frac{\partial}{\partial t}}{\pi^2}\right)\left(1 + \frac{\frac{l^2}{K}\frac{\partial}{\partial t}}{2^2\pi^2}\right)\cdots\left(1 + \frac{\frac{l^2}{K}\frac{\partial}{\partial t}}{n^2\pi^2}\right)\cdots C_1 \tag{65}$$

It may be emphasized here that the transition from (62) to (65) is simply a question of identifying the coefficients $\frac{1}{3!}$, $\frac{1}{5!}$, etc., in (62) with the sums of the various infinite series of constants obtained if (65) were multiplied out. This is most easily done by comparison with (63) and (64).

To solve (65) for C_1 find functions $A_1, A_2, \ldots A_n \ldots$ such that

$$\left(1 + \frac{\frac{l^2}{K}\frac{\partial}{\partial t}}{n^2\pi^2}\right) A_n = E \tag{66}$$

hence

$$A_n = E\left(1 + a_n e^{-K\frac{n^2\pi^2}{l^2}t}\right) \tag{67}$$

Using these values for $A_1, A_2, \ldots$ in a manner similar to the quantities $x_r^{(\alpha)}$, $x_r^{(\beta)}$, etc., in (23), it is now possible to get an infinite series of equations for C_1 and its derivatives corresponding to equations (24) in the finite case. Assuming that the method of elimination holds when the number of equations becomes infinite, the value of C_1 obtained is

$$C_1 = E\left[\alpha + \sum_1^\infty \beta_n e^{-K\frac{n^2\pi^2}{l^2}t}\right] \tag{68}$$

where $\alpha, \beta_1, \beta_2, \ldots \beta_n, \ldots$ are arbitrary constants. Substituting this value of C_1 in equation (61) and performing the operations indicated there, on collecting terms it will be found that

$$v = E\left[\alpha x + \sum_1^\infty \beta'_n e^{-K\frac{n^2\pi^2}{l^2}t} \sin \frac{n\pi}{l} x\right] \tag{69}$$

To determine α, it is known when the steady state is reached, *i.e.*, when $t = \infty$.

$$(v)_{t=\infty} = E\frac{x}{l} \tag{70}$$

Hence $\alpha = \frac{1}{l}$. This result might also have been obtained by tracing through the eliminations from (67) to (68), but this was not necessary.

Finally the last condition in (58) gives $v = 0$ when $t = 0$; hence

$$-\frac{Ex}{l} = \sum_1^\infty \beta'_n \sin \frac{n\pi}{l} x \tag{71}$$

and from this the values of the constants $\beta'_n \ldots$ can be obtained by the usual Fourier series method.

It may be interesting to compare this with Heaviside's method. He writes equation (57) in the form[9]

$$K\frac{\partial^2 v}{\partial x^2} = pv$$

the solution of which is by ordinary methods

$$v = A \cosh \sqrt{\frac{p}{K}} x + B \sinh \sqrt{\frac{p}{K}} x.$$

Then since $v = 0$ when $x = 0$, $A = 0$, and since $v = E$ when $x = l$,

$$B = \frac{E}{\sinh \sqrt{\frac{p}{K}} l.}$$

Hence

$$v = \frac{E \sinh \sqrt{\frac{p}{K}} x}{\sinh \sqrt{\frac{p}{K}} l}.$$

[9] Heaviside, "Electromagnetic Theory," vol. 2, p. 138 *et seq.*, except for some slight changes in notation and terminal conditions.

It is evident this equation corresponds to the quotient of (61) by (62). Heaviside's determination of the roots of $\sinh \sqrt{\frac{p}{K}}l$ then corresponds to writing equation (62) in the factorial form (65) and the summation over these roots in the expansion theorem corresponds to the solving of equations of the type (66) and the subsequent eliminations. It may be noticed that in solving the equations (66) two methods are available: (*a*) let $a_1, a_2, \ldots a_n \ldots$ in (67) be undetermined constants whose values are determined later, as has been done above; (*b*) assume that Heaviside's terminal conditions hold so that the value of each of the constants $a_1, a_2, \ldots a_n \ldots$ is -1. Then, on carrying out the elimination, a value for C_1 is obtained which does not contain any unknown constants, and knowing C_1, v is obtained from (61).

Following Heaviside it will be found very convenient in subsequent work to use a symbolical notation for the series developments that arise. It is not necessary to do so, but it will be found to curtail considerably the labor of writing. For example, (61) may be written,

$$\frac{1}{\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}}\left[x\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}+\frac{x^3}{3!}\left(\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\right)^3+\frac{x^5}{5!}\left(\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\right)^5+\cdots\right]C_1 \qquad (72)$$

and this by analogy with the expansion for $\sinh n\theta$, can be denoted symbolically by

$$\frac{1}{\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}}\sinh\left(x\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\right)C_1 \qquad (72a)$$

The factor $\frac{1}{\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}}$ in front gives rise to no difficulty, as it cancels out again when the sinh term is written in the factorial form

$$x\left(1+\frac{\frac{x^2}{K}\frac{\partial}{\partial t}}{\pi^2}\right)\left(1+\frac{\frac{x^2}{K}\frac{\partial}{\partial t}}{2^2\pi^2}\right)\cdots\left(1+\frac{\frac{x^2}{K}\frac{\partial}{\partial t}}{n^2\pi^2}\right)\cdots C_1 \qquad (72b)$$

The following abbreviations which will be required later are now self-evident.

$$\cosh\left(x\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\right)C_1 = \left(1 + \frac{x^2}{2!}\frac{1}{K}\frac{\partial}{\partial t} + \frac{x^4}{4!}\frac{1}{K^2}\frac{\partial^2}{\partial t^2} + \cdots\right)C_1 \qquad (73)$$

and

$$J_n\left(x\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\right)C_1 = \frac{x^n}{2^n\,\Gamma\,(n+1)}\left[1 - \frac{x^2}{2(2n+2)}\frac{1}{K}\frac{\partial}{\partial t} + \frac{x^4}{2.4(2n+2)\,(2n+4)}\frac{1}{K^2}\frac{\partial^2}{\partial t^2} + \cdots\right]C_1 \qquad (74)$$

where the factor z_0 in (55) has been replaced by $\frac{1}{2^n\,\Gamma\,(n+1)}$ to conform to the standard expression for the Bessel function. Both (73) and (74) can be written in a factorial form analogous to (72b).

FLOW OF HEAT IN A SEMI-INFINITE SOLID.

As the solution for an infinite or semi-infinite solid is usually given in the form of an integral instead of an infinite series, it may be well to show how this result is arrived at. The equations for the flow of heat in a semi-infinite solid are

$$K\frac{\partial^2 v}{\partial x^2} = \frac{\partial v}{\partial t} \qquad (75)$$

$$\left.\begin{aligned} v &= f(x) \text{ when } t = 0 \\ v &= 0 \text{ when } x = 0 \\ v &= 0 \text{ when } x = \infty \end{aligned}\right\} \qquad (75a)$$

Solving these equations in a manner similar to that used in the last example, and using the last condition in (75a) in the form $v = 0$ when $x = l$ as l tends to infinity. The result is [10]

$$v = \lim_{l\to\infty}\sum_{1}^{\infty} e^{-K\frac{n^2\pi^2}{l^2}t}\sin\frac{n\pi}{l}x.\frac{2}{l}\int_0^l f(x')\sin\frac{n\pi}{l}x'\,dx' \qquad (76)$$

and as $l \longrightarrow \infty$ this can be written as an integral, putting $\frac{\pi}{l} = d\alpha$

$$v = \frac{2}{\pi}\int_0^\infty e^{-K\alpha^2 t}\sin\alpha x\int_0^\infty f(x')\sin\alpha x'\,dx'\,d\alpha \qquad (76a)$$

[10] See Carslaw, "Introduction to Theory of Conduction of Heat," 1921, p. 35.

which corresponds with the expression given by Carslaw (*loc. cit.*). This again can be transformed as shown by him to the more standard form

$$v = \frac{1}{2\sqrt{\pi K t}} \int_0^\infty f(x') \left[e^{-\frac{(x-x')^2}{4Kt}} - e^{-\frac{(x+x')^2}{4Kt}} \right] dx'$$

FOURIER'S RING.

In order to illustrate the application of the method to Bessel functions, it is first necessary to solve the problem of Fourier's Ring. In this case the equations for the temperature are

$$K \frac{\partial^2 v}{\partial x^2} = \frac{\partial v}{\partial t} \quad (t > 0, \ -\pi < x < \pi) \tag{77}$$

$$v = f(x) \quad (t = 0, \ -\pi < x < \pi) \tag{78}$$

$$\left.\begin{aligned} (v)_{x=\pi} &= (v)_{x=-\pi} \\ \left(\frac{\partial v}{\partial x}\right)_{x=\pi} &= \left(\frac{\partial v}{\partial x}\right)_{x=-\pi} \end{aligned}\right\} \tag{79}$$

Integrating (77) from $-\pi$ to x,

$$\frac{\partial v}{\partial x} = \left(\frac{\partial v}{\partial x}\right)_{x=-\pi} + \frac{1}{K} \int_{-\pi}^{x} \frac{\partial v}{\partial t} dx \tag{80}$$

Integrating again

$$v = C + C_1(x + \pi) + \frac{1}{K} \int_{-\pi}^{x} \int_{-\pi}^{x} \frac{\partial v}{\partial t} dx\, dx. \tag{81}$$

where $C = (v)_{x=-\pi}$ and $C_1 = \left(\frac{dv}{dx}\right)_{x=-\pi}$ are functions of t alone. Solving this integral equation, the result may be written

$$v = \cosh\left[(x+\pi)\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\right] C + \frac{1}{\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}} \sinh\left[(x+\pi)\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\right] C_1 \tag{82}$$

Putting $x = 0$ in this expression

$$(v)_{x=0} = \cosh\left[\pi\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\right] C + \frac{1}{\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}} \sinh\left[\pi\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\right] C_1 \tag{83}$$

Returning again to equation (77) and integrating from $+\pi$ to x, the result is obtained,

$$v = \cosh\left[(x-\pi)\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\right] C + \frac{1}{\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}} \sinh\left[(x-\pi)\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\right] C_1 \tag{84}$$

where C and C_1 are the same as in (82) on account of the relations (79). Putting $x = 0$ in (84)

$$(v)_{x=0} = \cosh\left[-\pi\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\right]C + \frac{1}{\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}}\sinh\left[-\pi\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\right]C_1 \quad (85)$$

Subtracting (85) from (83), the cosh terms disappear and

$$0 = \frac{2}{\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}}\sinh\left[\pi\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\right]C_1 \quad (86)$$

Writing this in the factorial form

$$0 = \pi\left(1 + \frac{\pi^2\frac{1}{K}\frac{\partial}{\partial t}}{\pi^2}\right)\left(1 + \frac{\pi^2\frac{1}{K}\frac{\partial}{\partial t}}{2^2\pi^2}\right)\cdots\left(1 + \frac{\pi^2\frac{1}{K}\frac{\partial}{\partial t}}{n^2\pi^2}\right)\cdots C_1 \quad (87)$$

and finding functions $A_1, A_2, \ldots A_n \ldots$ such that

$$\left(1 + \frac{\frac{1}{K}\frac{\partial}{\partial t}}{n^2}\right)A_n = 0 \quad (88)$$

giving

$$A_n = a_n e^{-Kn^2t} \quad (89)$$

then on applying the method of elimination

$$C_1 = \sum_1^\infty a'_n e^{-Kn^2t} \quad (90)$$

where $a'_1, a'_2, \ldots a'_n \ldots$ are some new constants.

Again, on differentiating (82) and (84) with respect to x, and putting $x = 0$ in the result,

$$\left(\frac{\partial v}{\partial x}\right)_{x=0} = \sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\sinh\left[\pi\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\right]C + \cosh\left[\pi\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\right]C_1 \quad (91)$$

and

$$\left(\frac{\partial v}{\partial x}\right)_{x=0} = \sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\sinh\left[-\pi\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\right]C + \cosh\left[-\pi\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\right]C_1 \quad (92)$$

Subtracting these equations,

$$0 = 2\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\sinh\left[\pi\sqrt{\frac{1}{K}\frac{\partial}{\partial t}}\right]C \quad (93)$$

Writing this in the factorial form

$$0 = \frac{x}{K}\frac{\partial}{\partial t}\left(1 + \frac{\pi^2\frac{1}{K}\frac{\partial}{\partial t}}{\pi^2}\right)\left(1 + \frac{\pi^2\frac{1}{K}\frac{\partial}{\partial t}}{2^2\pi^2}\right)\cdots\left(1 + \frac{\pi^2\frac{1}{K}\frac{\partial}{\partial t}}{n^2\pi^2}\right)\cdots C \quad (94)$$

This is identical with equation (87) except for the extra factor $\frac{\partial}{\partial t}$ in front. This gives rise to a constant term in addition to the exponential, hence,

$$C = \sum_{0}^{\infty} b'_n e^{-Kn^2t} \tag{95}$$

Substituting the values of C and C_1 from (95) and (90) in (81), the value of v is obtained after some obvious simplifications in the standard form

$$v = \sum_{0}^{\infty} (\alpha_n \cos nx + \beta_n \sin nx) e^{-Kn^2t} \tag{96}$$

where α_n and β_n are determined in the usual manner from (78).

It may be remarked in connection with the subtraction and differentiation of the symbolic sines and cosines, etc., above, that these operations must be justified by recourse to the infinite series they represent. It will readily be noticed, however, that they follow the usual laws for these expressions.

FLOW OF HEAT IN AN INFINITE CYLINDER.

This example will illustrate the application to Bessel's function. Let the surface $r = a$ be kept at zero temperature, and the initial temperature be $v = f(r, \theta)$. The equation of conduction in this case is

$$\frac{\partial v}{\partial t} = K\left(\frac{\partial^2 v}{\partial r^2} + \frac{1}{r}\frac{\partial v}{\partial r} + \frac{1}{r^2}\frac{\partial^2 v}{\partial \theta^2}\right) \tag{97}$$

Writing this equation

$$\frac{\partial^2 v}{\partial \theta^2} = \frac{r^2}{K}\frac{\partial v}{\partial t} - r^2\frac{\partial^2 v}{\partial r^2} - r\frac{\partial v}{\partial r} \tag{98}$$

the same conditions hold for integration with respect to θ, as in the case of Fourier's ring, *i.e.*,

$$(v)_{\theta=\pi} = (v)_{\theta=-\pi} \tag{99}$$

$$\left(\frac{\partial v}{\partial \theta}\right)_{\theta=\pi} = \left(\frac{\partial v}{\partial \theta}\right)_{\theta=-\pi} \tag{100}$$

Hence proceeding as in that example

$$v = \cosh\left[(\theta+\pi)\sqrt{\frac{r^2}{K}\frac{\partial}{\partial t} - r^2\frac{\partial^2}{\partial r^2} - r\frac{\partial}{\partial t}}\right]C$$
$$+ \frac{1}{\sqrt{\frac{r^2}{K}\frac{\partial}{\partial t} - r^2\frac{\partial^2}{\partial r^2} - r\frac{\partial}{\partial r}}}\sinh\left[(\theta+\pi)\sqrt{\frac{r^2}{K}\frac{\partial}{\partial t} - r^2\frac{\partial^2}{\partial r^2} - r\frac{\partial}{\partial r}}\right]C_1 \tag{101}$$

and the equations analogous to (86) and (93) become,

$$0 = \frac{2}{\sqrt{\frac{r^2}{K}\frac{\partial}{\partial t} - r^2\frac{\partial^2}{\partial r^2} - r\frac{\partial}{\partial r}}} \sinh\left[\pi\sqrt{\frac{r^2}{K}\frac{\partial}{\partial t} - r^2\frac{\partial^2}{\partial r^2} - r\frac{\partial}{\partial r}}\right] C_1 \qquad (102)$$

and

$$0 = 2\sqrt{\frac{r^2}{K}\frac{\partial}{\partial t} - r^2\frac{\partial^2}{\partial r^2} - r\frac{\partial}{\partial r}} \sinh\left[\pi\sqrt{\frac{r^2}{K}\frac{\partial}{\partial t} - r^2\frac{\partial^2}{\partial r^2} - r\frac{\partial}{\partial r}}\right] C \qquad (103)$$

where

$$C = (v)_{\theta=\pi} \text{ and } C_1 = \left(\frac{\partial v}{\partial \theta}\right)_{\theta=\pi}$$

Writing (102) in the factorial form it becomes

$$0 = 2\pi\left(1 + \frac{\pi^2\left(\frac{r^2}{K}\frac{\partial}{\partial t} - r^2\frac{\partial^2}{\partial r^2} - r\frac{\partial}{\partial r}\right)}{\pi^2}\right)$$

$$\cdots\left(1 + \frac{\pi^2\left(\frac{r^2}{K}\frac{\partial}{\partial t} - r^2\frac{\partial^2}{\partial r^2} - r\frac{\partial}{\partial r}\right)}{n^2\pi^2}\right)\cdots C_1 \qquad (104)$$

and in order to apply the method of elimination functions A_1, A_2, $\ldots$ A_n $\ldots$ must be found such that

$$\left[1 + \frac{\pi^2\left(\frac{r^2}{K}\frac{\partial}{\partial t} - r^2\frac{\partial^2}{\partial r^2} - r\frac{\partial}{\partial r}\right)}{n^2\pi^2}\right]A_n = 0. \qquad (105)$$

or

$$\frac{\partial^2 A_n}{\partial r^2} + \frac{1}{r}\frac{\partial A_n}{\partial r} + \left(-\frac{1}{K}\frac{\partial}{\partial t} - \frac{n^2}{r^2}\right)A_n = 0. \qquad (106)$$

Solving this by the integral equation method already outlined in (50) *et seq.*,

$$A_n = J_n\left(r\sqrt{-\frac{1}{K}\frac{\partial}{\partial t}}\right)B \qquad (107)$$

where $B = (A_n)_{r=0}$ is a function of t alone.

By applying the method of elimination to (104) the value obtained for C_1 would be $\sum_1^\infty a_n A_n$ and in a similar manner from (103) C could be expressed as $\sum_1^\infty a'_n A'_n$. Substitution in (101) of these values gives

$$v = \sum_1^\infty a_n A_n f_n(\theta) + \sum_1^\infty a'_n A'_n f'_n(\theta) \qquad (108)$$

where A_n and A'_n are functions of r and t alone. But from the terminal conditions $v = 0$ when $r = a$. Hence when $r = a$, A_n and A'_n must both equal zero, since they are functions of t, and the presence of the arbitrary constants a_n and a'_n in (108) requires that each individual A_n vanish, instead of the coefficients of the various powers of t, which is more usually the case. Hence putting $r = a$ in (107),

$$0 = J_n\left(a\sqrt{-\frac{1}{K}\frac{\partial}{\partial t}}\right)B \tag{109}$$

It is known that $J_n(a\alpha)$ possesses equal positive and negative roots, and if the positive roots are $\alpha_1, \alpha_2, \ldots \alpha_s \ldots$, equation (109) can be written in the factorial form,

$$0 = Q\left[1 + \frac{\frac{1}{K}\frac{\partial}{\partial t}}{\alpha_1^2}\right]\left[1 + \frac{\frac{1}{K}\frac{\partial}{\partial t}}{\alpha_2^2}\right]\cdots\left[1 + \frac{\frac{1}{K}\frac{\partial}{\partial t}}{\alpha_s^2}\right]\cdots B \tag{110}$$

where Q is some constant. This equation which is similar to (87) has the solution,

$$B = \sum_1^\infty p_s e^{-K\alpha_s^2 t}$$

where $p_1, p_2, \ldots p_s \ldots$ are arbitrary constants. Substituting this value of B in equation (107) when written in the form

$$A_n = r^n\left[1 + \frac{r^2\frac{1}{K}\frac{\partial}{\partial t}}{2(2n+2)} + \frac{r^4\frac{1}{K^2}\frac{\partial^2}{\partial t^2}}{2.4(2n+2)(2n+4)} + \cdots\right]\sum_1^\infty p_s e^{-K\alpha_s^2 t} \tag{111}$$

and performing the operations, it becomes

$$A_n = \sum_{s=1}^{s=\infty} p'_s J_n(\alpha_s r) e^{-K\alpha_s^2 t} \tag{112}$$

From (104) and (106)

$$C_1 = \sum_{n=1}^{n=\infty} p''_s A_n$$

Hence

$$C_1 = \sum_{n=1}^{n=\infty}\sum_{s=1}^{s=\infty} p_{n,s} J_n(\alpha_s r) e^{-K\alpha_s^2 t} \tag{113}$$

In a similar manner the value of C is found from (103).

$$C = \sum_{n=0}^{n=\infty}\sum_{s=1}^{s=\infty} q_{n,s} J(\alpha_s r) e^{-K\alpha_s^2 t} \tag{114}$$

Substituting these values of C and C_1 in equation (101), written out in the power series expansion and performing the differentiations indicated, the final result is obtained in the standard form

$$v = \sum_{n=0}^{n=\infty} \sum_{s=1}^{s=\infty} \left(A_{n,s} \cos n\theta + B_{n,s} \sin n\theta \right) J_n(\alpha_s r) e^{-K\alpha_s^2 t} \qquad (115)$$

where $A_{n,s}$ and $B_{n,s}$ are determined in the usual way from the condition $v = f(r, \theta)$ when $t = 0$.

Several more examples of heat problems could be given, but those derived here should suffice to show the general method of procedure. For problems in the flow of electricity in continuous systems, Heaviside's Electromagnetic Theory will supply many results already worked out, which can be easily modified in accordance with the suggestions made at the end of the problem of a cable with resistance and capacity.

APPLICATION TO POTENTIAL PROBLEMS.

The similarity between the equations of conduction of heat and Laplace's equation suggests that this method might be used to solve potential problems. Its application, however, is accompanied by difficulties which are mainly due to the way in which the boundary conditions are stated. The following examples will make this clear.

THE POTENTIAL DUE TO TWO CONDUCTING PLANES INTERSECTING AT AN ANGLE $\frac{\pi}{p}$.

Assume there is no variation in the z direction, then $\frac{\partial^2 V}{\partial z^2} = 0$ and Laplace's equation in cylindrical coördinates may be written,

$$\frac{\partial^2 V}{\partial r^2} + \frac{1}{r}\frac{\partial V}{\partial r} + \frac{1}{r^2}\frac{\partial^2 V}{\partial \phi^2} = 0 \qquad (116)$$

subject to the conditions

$$\left.\begin{aligned} V &= V_0 \text{ when } \phi = 0 \\ V &= V_0 \text{ when } \phi = \frac{\pi}{p} \end{aligned}\right\} \qquad (117)$$

If $r\frac{d}{dr}$ is replaced by D_r, equation (116) may be written

$$\frac{\partial^2 V}{\partial \phi^2} = -D_r^2 V \qquad (118)$$

integrating twice with respect to ϕ

$$V = V_0 + C\phi - \int_0^\phi \int_0^\phi D_r^2 V \, d\phi \, d\phi \qquad (119)$$

where $C = \left(\frac{\partial V}{\partial \phi}\right)_{\phi=0}$ is a function of r alone, and V_0 is the value of V when $\phi = 0$. V_0 being thus a constant independent of r and ϕ does not give rise to a series of terms when the integral equation (119) is solved by successive approximations due to the presence of the differentiator D_r^2 under the integral sign. The solution of (119) becomes

$$V = V_0 + C\phi - \frac{\phi^3}{3!} D_r^2 C + \frac{\phi^5}{5!} D_r^4 C - \text{etc.} \tag{120}$$

or symbolically

$$V = V_0 + \frac{1}{D_r} \sin(\phi D_r) C \tag{121}$$

but from (117) $V = V_0$ when $\phi = \frac{\pi}{p}$. Substituting in (121) gives

$$0 = \frac{1}{D_r} \sin\left(\frac{\pi}{p} D_r\right) C \tag{122}$$

which may be written in the form of an infinite product,

$$0 = \frac{\pi}{p}\left(1 - \frac{\frac{\pi^2}{p^2} D_r^2}{\pi^2}\right)\left(1 - \frac{\frac{\pi^2}{p^2} D_r^2}{2^2\pi^2}\right) \cdots \left(1 - \frac{\frac{\pi^2}{p^2} D_r^2}{n^2\pi^2}\right) \cdots C \tag{123}$$

In order to apply the method of elimination, functions a_1, a_2, . . . a_n . . . must be found such that

$$\left(1 - \frac{\frac{\pi^2}{p^2} D_r^2}{n^2\pi^2}\right) a_n = 0 \tag{124}$$

or

$$r \frac{\partial}{\partial r}\left(r \frac{\partial a_n}{\partial r}\right) - p^2 n^2 a_n = 0 \tag{125}$$

the solution of which is

$$a_n = A_n r^{pn} + B_n r^{-pn} \tag{126}$$

Hence by elimination (123) gives

$$C = \sum_{n=1}^{n=\infty} (A_n' r^{pn} + B_n' r^{-pn}) \tag{127}$$

where A'_n and B'_n are some arbitrary constants.

Substituting this value of C in (120) and simplifying

$$V = V_0 + \sum_{n=1}^{n=\infty} (A_n'' r^{pn} + B_n'' r^{-pn}) \sin pn\theta \tag{128}$$

Now since $V = V_0$ when $r = 0$ each of the coefficients B''_1, B''_2 . . . B''_n . . . must be zero, hence

$$V = V_0 + \sum_{n=1}^{n=\infty} A''_n r^{pn} \sin pn\theta \tag{129}$$

Another boundary condition is required to determine the remaining constants. This will be taken to be that the potential over the sphere at infinity is a constant, and equal to V_1. Hence

$$V_1 = V_0 + \lim_{l\to\infty} \sum_{n=1}^{n=\infty} A''_n l^{pn} \sin pn\theta \tag{130}$$

or

$$\operatorname*{Lim}_{l\to\infty} \left(\frac{V_1}{l^p} - \frac{V_0}{l^p}\right) = \lim_{l\to\infty} \left(A''_1 \sin p\theta + A''_2 l^p \sin 2p\theta + \cdots\right) \tag{131}$$

Now V_0 is some finite quantity so that $\frac{V_0}{l^p}$ tends to zero as $l \longrightarrow \infty$. If it is also assumed that V_1 is finite, $\frac{V_1}{l^p}$ tends to zero at the same time, so that all the coefficients are zero and the solution becomes trivial. If, however, $\frac{V_1}{l^p}$ tends to a constant finite value R as $l \longrightarrow \infty$, then

$$R = A''_1 \sin p\theta + A''_2 l^p \sin 2p\theta + A''_3 l^{2p} \sin 3p\theta + \cdots \tag{132}$$

and this holds for $0 < \theta < \frac{\pi}{p}$, and for the limit $l \longrightarrow \infty$.

By comparing this series with the expansion

$$\frac{\pi}{4} = \sin x + \frac{\sin 3x}{3} + \frac{\sin 5x}{5} + \cdots \tag{133}$$

which is valid in the region $0 < x < \pi$ the following equations are obtained where the limit $l \longrightarrow \infty$ is understood,

$$\begin{array}{lll} A''_1 = k & A''_3 l^{2p} = \frac{1}{3} k & A''_5 l^{4p} = \frac{1}{5} k \\ A''_2 = 0 & A''_4 = 0 & A''_6 = 0 \end{array} \quad \text{etc.}$$

where k is a constant. Hence from (129)

$$V = V_0 + \lim_{l\to\infty} \left(kr^p \sin p\theta + \frac{k}{3l^{2p}} r^{3p} \sin 3p\theta + \cdots\right) \tag{134}$$

or

$$V = V_0 + kr^p \sin p\theta \tag{135}$$

If $V = 0$ and $k = 1$, this becomes

$$V = r^p \sin p\theta \tag{136}$$

which corresponds with the well-known result.

Equation (136), however, does not give a constant potential over the sphere at infinity, which was assumed as one of the boundary conditions. The explanation is seen in (134). For all finite values of r this is equal to (135), but when $r = l$ and both approach the value infinity, the value of (134) becomes

$$V = V_0 + \lim_{r \to \infty} r^p \times \text{a constant.} \tag{137}$$

The usual method of deriving (136) by conformal representation does not show that this limitation exists.

THE GREEN'S FUNCTION FOR THE SPACE BOUNDED BY TWO PARALLEL PLANES $z = 0$ AND $z = C > 0$.

Take Laplace's equation in cylindrical coördinates z, ρ, θ. Let the pole be at the point z', 0, 0, and since there is circular symmetry $\frac{\partial V}{\partial \theta} = 0$, so that Laplace's equation becomes

$$\frac{\partial^2 V}{\partial r^2} + \frac{1}{r}\frac{\partial V}{\partial r} + \frac{\partial^2 V}{\partial z^2} = 0 \tag{138}$$

Integrating with respect to z,

$$\frac{\partial V}{\partial z} - \left(\frac{\partial V}{\partial z}\right)_{z=0} = -\int_0^z \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r}\right) V dz \tag{139}$$

writing $\left(\frac{\partial V}{\partial z}\right)_{z=0} = R$ which is a function of r alone, and integrating again

$$V = Rz - \int_0^z \int_0^z \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r}\right) V \, dz \, dz \tag{140}$$

since $(V)_{z=0} = 0$. This has the solution

$$V = \frac{1}{\sqrt{\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r}}} \sin\left(z\sqrt{\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r}}\right) R \tag{141}$$

But $(V)_{z=C} = 0$, so that this equation can be solved by finding functions $A_1, A_2, \ldots A_n, \ldots$ such that

$$\left[1 - \frac{C^2\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r}\right)}{n^2\pi^2}\right] A_n = 0 \tag{142}$$

or

$$\frac{\partial^2 A_n}{\partial r^2} + \frac{1}{r}\frac{\partial A_n}{\partial r} - \frac{n^2\pi^2}{C^2} A_n = 0 \tag{143}$$

The solution of this equation which has a zero at infinity is

$$A_n = K_0\left(\frac{n\pi}{C} r\right) \tag{144}$$

Hence by elimination

$$V = \sum_1^\infty a_n \sin \frac{n\pi}{C} z K_0\left(\frac{n\pi}{C} r\right) \tag{145}$$

where the constants a_n have to be determined from the fact that when $z = z'$, and r is very small, the value of V tends to $\frac{1}{r}$ — a constant.

Now a well-known integral is

$$\frac{2}{\pi}\int_0^\infty \cos \alpha z K_0(\alpha\rho) d\alpha = \frac{1}{(\rho^2 + z^2)^{\frac{1}{2}}} \tag{146}$$

which becomes, when $z = 0$,

$$\int_0^\infty K_0(\alpha\rho) d\alpha = \frac{\pi}{2}\frac{1}{\rho} \tag{147}$$

If in (145) a_n is taken equal to $\dfrac{1}{\sin \dfrac{n\pi}{C} z'}$, then putting $z = z'$ in this equation, and making r very small, it can be written

$$V_{\text{pole}} = \lim_{r \to 0} \sum_1^\infty \frac{1}{\frac{n\pi r}{C}} K_0\left(n\frac{\pi r}{C}\right) \cdot \frac{\pi r}{C} \tag{148}$$

$$= \frac{C}{\pi r}\int_0^\infty K_0(\alpha)\, d\alpha = \frac{C}{2r}. \tag{149}$$

Hence

$$V = \frac{2}{C}\sum_1^\infty \frac{\sin \frac{n\pi}{C} z}{\sin \frac{n\pi}{C} z'} K_0\left(\frac{n\pi}{C} r\right) \tag{150}$$

would give an expression which satisfies the conditions for a Green's function. Owing, however, to the presence of $\sin \frac{n\pi}{C} z'$ in the denominator, there will in general be other infinities, which

makes it desirable to find another form. To do this put $a_n = \sin \frac{n\pi}{C} z'$. Then (145) becomes when $z = z'$ and $r \longrightarrow 0$,

$$V_{\text{pole}} = \lim_{r \to 0} \frac{1}{2\frac{\pi r}{C}} \sum_1^\infty \left(1 - \cos \frac{2n\pi}{C} z'\right) K_0\left(n \frac{\pi r}{C}\right) \frac{\pi r}{C}$$

$$= \lim_{r \to 0} \left[\frac{C}{4r} - \frac{C}{2\pi r} \sum_1^\infty \cos\left(\frac{n\pi r}{C} \cdot \frac{2z'}{r}\right) K_0\left(n \frac{\pi r}{C}\right) \frac{\pi r}{C}\right] \tag{151}$$

$$= \lim_{r \to 0} \left[\frac{C}{4r} - \frac{C}{2\pi r} \int_0^\infty \cos\left(\alpha \frac{2z'}{r}\right) K_0(\alpha)\, d\alpha\right]$$

$$= \lim_{r \to 0} \left[\frac{C}{4r} - \frac{C}{2\pi r} \cdot \frac{\pi}{2} \cdot \frac{1}{\left(1 + \frac{4z'^2}{r^2}\right)^{\frac{1}{2}}}\right]$$

$$= \lim_{r \to 0} \left[\frac{C}{4r} - \frac{C}{8z'}\right] \tag{152}$$

Hence

$$V = \frac{4}{C} \sum_1^\infty \sin \frac{n\pi}{C} z' \sin \frac{n\pi}{C} z\, K_0\left(\frac{n\pi}{C} r\right) \tag{153}$$

is a suitable expression for the Green's function.[11]

THE POTENTIAL BETWEEN TWO PARALLEL CONDUCTING PLANES GIVEN BY $x = 0$ AND $x = l$.

This example is taken to show the failure of the method and suggest a possible approximate solution. Take Laplace's equation in rectangular coördinates,

$$\frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2} = 0 \tag{154}$$

The conditions of integration are

$$\left.\begin{aligned} V &= V_0 \text{ when } x = 0 \\ V &= V_1 \text{ when } x = l \end{aligned}\right\} \tag{155}$$

Integrating (154) in the usual manner with respect to x

$$V = V_0 + Cx - \int_0^x \int_0^x \left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) V\, dx\, dx \tag{156}$$

the solution of which may be written symbolically

$$V = V_0 + \frac{1}{\sqrt{\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}}} \sin\left(x \sqrt{\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}}\right) C \tag{156a}$$

[11] *Cf.* Gray and Matthews, "Bessel Functions," 1922, 2nd ed., p. 104.

where $C = \left(\frac{\partial V}{\partial x}\right)_{x=0}$. Putting $x = l$ and writing this equation in the factorial form, it becomes

$$V_1 - V_0 = l\left(1 - \frac{l^2\left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)}{\pi^2}\right)\left(1 - \frac{l^2\left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)}{2^2\pi^2}\right)\ldots C \quad (157)$$

To solve this, functions $a_1, a_2, \ldots a_n \ldots$ must be found such that

$$\left(1 - \frac{l^2\left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)}{n^2\pi^2}\right)a_n = V_1 - V_0 \quad (158)$$

or

$$\frac{\partial^2 a_n}{\partial y^2} + \frac{\partial^2 a_n}{\partial z^2} - \frac{n^2\pi^2}{l^2}a_n = \left(V_0 - V_1\right)\frac{n^2\pi^2}{l^2} \quad (159)$$

Integrating with respect to y

$$a_n = (V_0 - V_1) + (a_n)_{y=0} + \left(\frac{\partial a_n}{\partial y}\right)_{y=0} y + \int_0^y\int_0^y \left(\frac{n^2\pi^2}{l^2} - \frac{\partial^2}{\partial z^2}\right)a_n\, dy\, dy \quad (160)$$

which on solution by the method of successive approximations gives

$$a_n = (V_0 - V_1) + \cosh\left(y\sqrt{\frac{n^2\pi^2}{l^2} - \frac{\partial^2}{\partial z^2}}\right)(a_n)_{y=0} + \frac{1}{\sqrt{\frac{n^2\pi^2}{l^2} - \frac{\partial^2}{\partial z^2}}}\sinh\left(y\sqrt{\frac{n^2\pi^2}{l^2} - \frac{\partial^2}{\partial z^2}}\right)\left(\frac{\partial a_n}{\partial y}\right)_{y=0} \quad (161)$$

Now (161) is a differential equation containing two variables, $(a_n)_{y=0}$ and $\left(\frac{\partial a_n}{\partial y}\right)_{y=0}$, both functions of z. Hence another equation is required. It would seem as if this could be obtained from the conditions that with charges in the finite portion of space, the potential at infinity in both positive and negative directions must be zero. This would supply two conditions, one of which might be used in (160) if the integration were taken from $-l$ to y, then as l tends to infinity $(a_n)_{y=-l}$ tends to zero. Equation (161) would then have only one variable $\left(\frac{\partial a_n}{\partial y}\right)_{y=-l}$ and putting $y = +l$ in this equation, the method of elimination could be used to determine $\left(\frac{\partial a_n}{\partial y}\right)_{y=-l}$. On taking the limit of the series thus obtained as l tends to infinity, it will be found to be expressible as a definite integral similar to that obtained in the example of

flow of heat in a semi-infinite solid. This will not be done here, however, as the difficulty which the determination of the constants in the final result presents, can be illustrated as well in the two dimensional case as in the three dimensional problem. In the case of two dimensions $\frac{\partial^2 V}{\partial z^2} = 0$, hence (159) may be written,

$$\frac{\partial^2 a_n}{\partial y^2} = \frac{n^2\pi^2}{l^2}\left(a_n + V_0 - V_1\right) \tag{162}$$

The solution of which is

$$a_n = V_1 - V_0 + A_n \cosh \frac{n\pi}{l} y + B_n \sinh \frac{n\pi}{l} y \tag{163}$$

Hence from (157)

$$C = K(V_1 - V_0) + \sum_{n=1}^{n=\infty} \left(A_n' \cosh \frac{n\pi}{l} y + B_n' \sinh \frac{n\pi}{l} y\right) \tag{164}$$

and substituting this value of C in (156a)

$$V = V_0 + K'(V_1 - V_0)x + \sum_{n=1}^{n=\infty} \left(A_n'' \cosh \frac{n\pi}{l} y + B_n'' \sinh \frac{n\pi}{l} y\right) \sin \frac{n\pi}{l} x \tag{165}$$

and since the solution obtained must tend to zero as $y \longrightarrow \infty$ by expanding the hyperbolic sines and cosines, it is found that if the $e^{\frac{n\pi}{l} y}$ terms disappear $A_n'' = -B_n''$, giving

$$V = V_0 + K'(V_1 - V_0) + \sum_{1}^{\infty} A_n'' e^{-\frac{n\pi}{l} y} \sin \frac{n\pi}{l} x \tag{166}$$

for $y > 0$ and similarly

$$V = V_0 + K'(V_1 - V_0) + \sum_{1}^{\infty} A_n'' e^{\frac{n\pi}{l} y} \sin \frac{n\pi}{l} x \tag{167}$$

for $y < 0$.

If V_0 and V_1 both equal zero, then for $y > 0$

$$V = \sum_{1}^{\infty} A_n'' e^{-\frac{n\pi}{l} y} \sin \frac{n\pi}{l} x \tag{168}$$

The determination of the constants A_n'' presents the real difficulty. So far nothing has been said of the disposition of the charges or

charged conductors in the field. Suppose that, for instance, the cylinder represented by

$$(x-\alpha)^2+(y-\beta)^2=\delta^2$$

has a potential V_c and there are no other charges in the space. It seems as if this condition should suffice to determine analytically the values of the constants, but the problem of doing this has apparently not been solved. An approximate method, however, suggests itself. Let p points be taken on the surface of this cylinder. Then if the p values of x and y for these points are substituted in (168) and the first p terms of the series taken, the values of the coefficients $A_1 \ldots A_p$ could be obtained from the p equations; and provided the terms decrease in regular order, and the last term is small, this would give an approximate solution which could be used in the region where the value of the last term remained small enough to be negligible. Similarly if a line charge is placed at x', y', by surrounding this with a small cylinder, the potential on this cylinder will be practically uniform and equal to $\frac{1}{r}$, where r is the distance from x', y', if there are no other charges present. From the value of the potential at p points on this circumference the values of the coefficients might be determined as above. When several conductors are in the space, by taking sufficient numbers of points on each of them, it is probable that fairly good approximations might be obtained. This will, however, have to be tested by actual numerical work in known cases, to determine the value of the method.

EVALUATION OF DEFINITE INTEGRALS.

The operators which have been developed earlier in this work may sometimes be of use in determining the values of definite integrals. Take, for example,

$$I=\int_0^\infty e^{-xt}J_0(bx)\,dx \tag{169}$$

When $n=0$ equation (56) becomes with a slight change in notation

$$\left(1+x^2\int_0^b\frac{1}{b}\int_0^b b\,db\,db\right)J_0(bx)=1$$

so that if it is possible to introduce this operator under the integral sign, the Bessel function will be replaced by unity, and the integral

$\int_0^\infty e^{-xt}\,dx$ is then easily found. Differentiating (169) twice with respect to t gives

$$\frac{\partial^2 I}{\partial t^2} = \int_0^\infty x^2 e^{-xt} J_0(bx)\,dx \tag{170}$$

Hence

$$I + \int_0^b \frac{1}{b}\int_0^b b\,\frac{\partial^2 I}{\partial t^2}\,db\,db = \int_0^\infty e^{-xt}\left[\left(1 + x^2\int_0^b \frac{1}{b}\int_0^b b\,db\,db\right) J_0(bx)\right] dx$$
$$= \int_0^\infty e^{-xt}\,dx = \frac{1}{t} \tag{171}$$

Therefore

$$I = \frac{1}{t} - \int_0^b \frac{1}{b}\int_0^b b\,\frac{\partial^2 I}{\partial t^2}\,db\,db \tag{172}$$

and on solving this by successive approximations

$$I = \frac{1}{t} - \frac{b^2}{2^2}\frac{2!}{t^3} + \frac{b^4}{2^2.4^2}\frac{4!}{t^5} - \frac{b^6}{2^2.4^2.6^2}\frac{6!}{t^7} + \cdots$$
$$= \frac{1}{(t^2 + b^2)^{\frac{1}{2}}}$$

which is a well-known result.

In volume 3, p. 234 *et seq.*, of "Electromagnetic Theory," Heaviside gives a method of finding integrals in a similar manner, which is in fact very much shorter than the one just outlined. He uses, however, the opposite operator to the one used above, *i.e.*, he uses an operator which transforms a constant into the Bessel function, and as this involves the use of his "unit function," it cannot be discussed here. Several examples will be found in his book.

CONCLUSION.

The examples which have been worked out should be sufficient to show how the solution of some of the equations of mathematical physics and engineering can be made to depend upon the solution of an equation of the first order. All the problems given here are well known, but it is to be hoped that this method will be of assistance in obtaining new solutions. In the actual working of problems it will soon be found that many of the steps introduced above for the purpose of demonstrating the method may be omitted. For instance, after a little practice, the symbolical solution of most of the equations can be written down at sight instead of going through the formality of solving by the use of

an integral equation. Other simplifications will suggest themselves and shorten the writing considerably.

Fredholm, in his researches on integral equations, showed that an integral equation of the second kind could be regarded as the limit of a system of algebraic equations when the number of equations become infinite. It would appear from the results obtained here that this proposition may be a particular case of a more general one, which is that the solution of certain partial differential equations with n independent variables may be regarded as the solution of an ∞^n system of algebraic equations. For instance, in deriving the result for the flow of heat in an infinite cylinder given in (115), the method of elimination was applied twice, which corresponds to the solving of an ∞^2 system of algebraic equations; and the solutions for the transcendental functions themselves give a total of an ∞^3 system. Although the three transcendental functions give rise to a triply infinite system, this can still be regarded as an ∞^1 system. This generalization of Fredholm's theorem must be regarded as a suggestion and as not in any way proved.

In conclusion the writer wishes to thank Dr. E. J. Berg, whose interest in the work of Heaviside suggested this paper, for his suggestions in the course of the work, and also Dr. F. W. Grover, who read the manuscript, for his assistance. The debt owed to the writings of Heaviside may be plainly seen throughout the course of the paper.

Protein Value of Peanut Flour. WALTER H. EDDY and RENA S. ECKMAN, of Columbia University (*J. Biol. Chem.*, 1923, **55**, 119-129), have used peanut flour as a constituent of rations fed to rats. Their results demonstrate that the protein of peanut flour has a high biological and food value, and is an excellent supplement for the protein of wheat flour. Peanut flour is slightly superior to meat as a growth producer. J. S. H.

New Occurrence of Celestite. SAMUEL G. GORDON (*Proc. Acad. Nat. Sciences*, 1922, **74**, 110–111) reports the occurrence of small brilliant colorless crystals of celestite or native strontium sulphate at the famous zinc mines at Franklin, New Jersey. J. S. H.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

LATHE BREAKDOWN TESTS OF SOME MODERN HIGH-SPEED TOOL STEELS.[1]

By J. H. French and Jerome Strauss.

[ABSTRACT.]

THIS report is concerned with comparisons of performance of modern high-speed tool steels in so-called "lathe breakdown tests," in which endurance of tools is measured under definite working conditions, and likewise with the limitations of this method when applied to the purchase of steel. The modern steels are first classified according to chemical composition, and this division is made use of in discussion of results obtained.

Important features developed or conclusions drawn may be summarized as follows:

1. Breakdown tests are not satisfactory as the basis of purchase for high-speed tool steels.

2. While competitive comparisons of brands of nearly similar performance are not justified, owing to the qualitative nature of this type of test, relatively large differences may be ascertained with certainty, providing sufficient tools are tested and averages of at least two grinds are used in interpretation of results.

3. In certain severe breakdown tests with roughing tools on 3 per cent. nickel steel forgings, in which high frictional temperatures were produced, it was found that the performance of commercial low tungsten-high vanadium and cobalt steels was superior to that of the high tungsten-low vanadium type, and special steels containing about ¼ per cent. uranium or ¾ per cent. molybdenum. The average power consumption in all cases was practically the same, so that this factor need not be introduced in comparisons which may be made on the basis of endurance of the tools.

4. Modification in test conditions, including small changes in tool angles but principally changes in cutting speed, more markedly affected the performance of steels containing cobalt or special

* Communicated by the Director.

[1] Technologic Paper, No. 228, price fifteen cents.

elements such as uranium or molybdenum than that of the basic types (plain chromium-tungsten-vanadium steels).

5. The relatively poor endurance of the high-tungsten steels under severe working conditions was not observed in more moderate tests which were made on the same test log with equal cutting speed and depth of cut, but with reduced feed, and in which the frictional temperatures produced were not so high. Also in these latter tests the performance of the cobalt steels was better than either the low or high-tungsten steels.

6. Hardness determinations and examination of fractures indicate that the various types of commercial high-speed steel show differences in behavior under heat treatment and in physical properties which probably are of importance under moderate working conditions, and might counterbalance slight advantages in performance.

METHODS OF MEASURING THE PLASTICITY OF CLAYS.[3]

By F. P. Hall.

[ABSTRACT.]

PROBABLY the most characteristic property of clay is plasticity, yet there is at present no perfectly satisfactory method of measuring it. This is probably due to the difficulty of defining plasticity in terms that are capable of mathematical expression. Numerous methods have been proposed for measuring this property and certain criticisms concerning the more important methods are given in the first part of this paper. The second part is devoted to the presentation of experimental data collected with the use of the Bingham plastometer, an instrument that has been recently brought forward for the measurement of plasticity of paints, greases, and other semi-rigid materials. The plastometer is a modified capillary viscosimeter.

Plasticity has been resolved into its two components by Bingham, and the Bingham plastometer is supposed to give a measure of these two components designated as yield value and mobility. A certain equation has been developed by Bingham giving the relation between the two factors of plasticity of a material and the dimensions of the capillary of tube used in the plastometer. This equation, together with a modification, has been proven by Bingham to hold for paints but in the case of clay

[3] Technologic Paper, No. 234, price ten cents.

slips with which we are dealing the equation does not hold true, as is shown in this article. This is due to an end effect which is not taken into account in the equations, and which we have not been able to evaluate. Thus we have not been able to express these two factors, *viz.*, yield value and mobility in absolute units. But by using the same capillary we have been able to obtain some interesting comparisons of several types of clays and the effect of addition of certain materials and reagents to clay slip. We believe that by using the same capillary we can determine in a comparative manner the relative plasticities of clays.

NEW MOLLIER CHART FOR AMMONIA.[3]

A COMPUTING chart has just been issued by the Bureau of Standards for the use of refrigeration experts. This chart embodies the results of an extensive series of measurements of the thermodynamic properties of ammonia. To make the results of these investigations available for use by refrigerating engineers, ammonia tables, similar to the familiar steam tables, have been computed and prepared for publication. These data are also given graphically in the form of a "Mollier" chart. Numerous forms of such charts have been published, not only for steam and ammonia, but for other materials. The arrangement of the present chart is believed to possess certain advantages over previous forms. The coördinates are pressure (plotted to a logarithmic scale) as ordinates, and heat content as abscissa. The chart measures 10½ inches high by 25 inches wide—a convenient size for desk use. Lines of constant entropy, volume, temperature, and quality are drawn on the chart. The chart is printed in black ink only. The arrangement is such that all lines are clearly distinguishable and can be readily recognized and followed, thus avoiding two-color printing and its attendant loss in accuracy.

Pressures and volumes can easily be read to an accuracy of 1 per cent. and heat content to within 0.5 Btu. By the use of the chart it is possible to analyze the processes occurring in a refrigerating cycle, and to determine, for example, the work of compression, the heat absorbed by the ammonia evaporated, the volume of the vapor at various stages of the cycle, etc. In all

[3] Miscellaneous Publication, No. 52, price five cents.

cases except where very accurate work is required the chart is a complete substitute for the tables and results can be obtained from it with greater ease and speed than are possible with the tables. The use of the chart is explained in detail in Bureau of Standards Circular No. 142, which contains the ammonia tables.

SOLDER FOR ALUMINUM.[4]

MOST of the metals commonly used in solders, except magnesium, are electropositive to aluminum, so that any metals used in making a soldered joint of aluminum act electrolytically in the presence of moisture as positive galvanic poles, accelerating the corrosion of the aluminum. Magnesium can not be utilized advantageously even though it is electronegative to aluminum because the metal disintegrates rapidly in the presence of moisture. Soldered joints of aluminum which are to be exposed to moisture should be protected against corrosion by a paint or varnish.

Various compositions of zinc-tin and zinc-tin-aluminum solders give the best results. The tensile strength of a good aluminum solder is about 7000 lbs.-in.^{2}, for those with higher tensile strength have, in general, their temperature of complete liquation too high for soldering purposes. As a rule the strength of an aluminum soldered joint depends upon the type and upon the workmanship.

ERRATA.

SOLUBILITY OF MANNITE IN MIXTURES OF ETHYL ALCOHOL AND WATER.

BY

HENRY JERMAIN MAUDE CREIGHTON

AND

DAVID S. KLAUDER, JR.

MAY, 1923, JOURNAL.

Page 687, lines sixteen and seventeen should read:

$$d^{25°}_{4°ac} = 0.78509$$

$$n^{25°}_{D} = 1.35954$$

[4] Circular No. 78, price five cents.

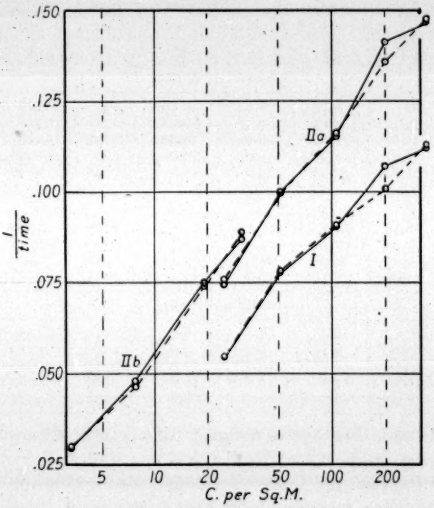
NOTES FROM THE LABORATORY OF PURE SCIENCE, NELA RESEARCH LABORATORIES.*

THE RELATION BETWEEN FIELD BRIGHTNESS AND THE SPEED OF RETINAL IMPRESSION.

By Percy W. Cobb.

THE time values (t) of the table represent the times of exposure of a black circular dot in the centre of a white screen,

FIG. 1



Reciprocal of weighted mean threshold time, as given in Table I, 1/t, plotted against the logarithm of the brightness. Curve I, seven subjects. Curves II, for subjects *A*, *I*, and *S* in high (*a*) and low (*b*) ranges of brightness as in Table I.
———— solid lines, "light" series (*L*).
– – – – – – – – broken lines, "dark" series (*D*).

necessary in order that the subject may correctly state whether or not the dot has been actually shown, the purpose of the work being to show how these time values change with changes in the

* Communicated by the Director.

illumination. A detailed description of the apparatus used to produce such a test stimulus appears in the original and in prior communications therein cited. The experiments were conducted with seven subjects over a fairly high range of illuminations with the results (t) given in the table. In the figure are plotted the reciprocals of these time values as given in the right-hand section of the table, $1/t$. Three of the subjects were investigated over a lower range of illuminations, their results for the two ranges being given in sections a and b of the table, respectively, and being plotted in curves IIa and IIb, Fig. 1.

The subjects varied rather widely in the absolute minimum

TABLE I.

C. per Sq. M.	Ml.	t			$1/t$		
		L	D	M	L	D	M
(a)	Subjects A, I, and S						
342	107	6.79	6.82	6.80	.147	.148	.148
201	63.1	7.08	7.38	7.23	.141	.136	.138
105	33.0	8.71	8.61	8.66	.115	.116	.116
51.5	16.2	9.95	10.05	10.0	.100	.0996	.0998
24.8	7.8	13.4	13.2	13.3	.0748	.0760	.0754
(b)							
31.3	8.83	11.5	11.2	11.4	.0867	.0889	.0878
18.9	5.95	13.3	13.5	13.4	.0750	.0741	.0746
7.73	2.43	20.9	21.5	21.2	.0478	.0466	.0472
3.33	1.05	34.0	33.3	33.6	.0294	.0301	.0298
		Seven Subjects					
342	107	8.9	8.8	8.8	.112	.113	.112
201	63.1	9.4	9.9	9.6	.107	.101	.104
105	33.0	11.1	10.9	11.0	.0904	.0916	.0910
51.6	16.2	12.9	12.8	12.8	.0776	.0782	.0779
24.8	7.8	16.9	16.8	16.8	.0592	.0594	.0593

time required. The average times for all light conditions compared varied from 7.3 to 28.7 δ for the several subjects. The difference between the L and D values (see explanation of table) is not more than is probable as chance variation.

The geometric mean time of darkening of a circular spot 4.24 mm. in diameter, at 6.01 metres distance, necessary in order that a threshold impression may result.

The sub-heading L means extensive bright surroundings ($46.6 \times 47.6°$ in the visual field); D, bright surroundings restricted ($5.8 \times 5.2°$), the remainder being dark; M, the mean of the L and D values.

Brightness is stated in candles per square metres and in millilamberts; and the fields indicated by L and D were kept as nearly as possible uniform with the area about the stimulus.

The times (t) are stated in thousandths of a second (δ). The reciprocals of these ($1/t$) are plotted in Fig. 1.

AN INTERCOMPARISON OF THE HIGH TEMPERATURE SCALES IN USE IN THIS COUNTRY WITH THOSE IN USE IN ENGLAND.

By W. E. Forsythe.

SEVERAL years ago Nela Research Laboratory sought an intercomparison of its high temperature scale with those of the Bureau of Standards, the Physical Laboratory of the University of Wisconsin and the Research Laboratory of the General Electric Company at Schenectady through measurements in each of the laboratories on several tungsten filament lamps specially prepared in this laboratory. The results obtained, as presented before this Society in 1917,[1] showed a very good agreement. Since that time the intercomparison has been extended to include the National Physical Laboratory of London through the courtesy of Sir J. E. Petavel. Doctor Stratton of the Bureau of Standards kindly agreed also to have measurements made on the same lamps, and the results obtained in those two laboratories, together with the values found in Nela Research Laboratory, are given in Table I.

TABLE I.

Intercomparison of Temperature Scales of National Physical Laboratory, Bureau of Standards, and Nela Research Laboratory.

($c_2 = 14{,}350\mu \times$ deg.: $\lambda = 0.665\mu$: melting point of Au. = 1336° K. and melting point of Pd. = 1828° K.).

Lamp.	Current.	N. R. L. April, '20.	N. P. L. April, '22.	N. R. L. June, '22.	B. of S. Jan., '23.	N. R. L. Jan., '23.
T—77—B	5.2	1410° K.	1405° K.	1406° K.	1401° K.	1401° K.
	6.7	1599	1597	1595	1596	1591
	8.5	1796	1794	1794	1792	1791
	11.7	2106	2106	2104	2105	2104
T—78—C	15.4	1825	1825	1826	1824	1828
	20.4	2262	2266	2266	2265	2269
	27.4	2746	2758	2753	2755	2755

[1] *Phys. Rev.*, 2 S II, p. 139 (1918).

Less weight is to be given to the first set of measurements made in Cleveland in April, 1920, owing to the fact that the lamps were burned for many hours at high temperatures between the time of these measurements and the observations at the National Physical Laboratory reported in the fourth column of the table.

It is gratifying to note that the high temperature scales in use in England and in the United States are in such excellent agreement.

THE RELATION BETWEEN THE ELECTRICAL CONDUCTIVITY OF THE EXTERNAL MEDIUM AND THE RATE OF CELL-DIVISION IN SEA-URCHIN EGGS.

By R. S. Lillie and Ware Cattell.

THE resemblances between the patterns formed by the spindle-fibres and astral radiations of dividing cells and by the lines of force in electric and magnetic fields, together with other facts of cell-physiology, have suggested to physiologists the possibility that electrical factors play a fundamental part in cell-division, just as they almost certainly do in many other protoplasmic processes, especially the transmission of the state of excitation from region to region in irritable tissues such as nerve and muscle. It has been found, for example, that the velocity of transmission in the nerve-net of medusæ and in various types of musculature is a direct function (within a certain range of concentration and osmotic pressure) of the electrical conductivity of the medium. This observation is consistent with the hypothesis, supported by various other facts, that electric ("bioelectric") currents passing from one region to another of the irritable cell or nerve fibre through the external medium determine the spread of excitation in such tissues. If this is true, it might be expected that the rate of other protoplasmic processes which involve transmission of physiological influence through a distance might also be controlled by varying the electrical conductivity of the medium.

We have determined the relation between the electrical conductivity of the medium and the rate of cell-division in the eggs of the sea-urchin Arbacia, using mixtures of sea-water and isotonic sugar solutions. The eggs divide normally in these mixtures until the proportion of sea-water is reduced to 20 or 25 volumes per cent. From this concentration down to a concentration of about 5 volumes per cent. sea-water the rate of division

becomes progressively slower as the dilution increases. When the eggs are returned to sea-water they resume their normal rate of division and develop to swimming larvæ. In the less dilute mixtures, down to about 30 volumes per cent. sea-water, the rate of division remains almost the same as in undiluted sea-water. The external conductivity can therefore be reduced to a third of the normal without significantly altering the rate of division. In the media of lower conductivity (20 to 5 volumes per cent.) division becomes slower as conductivity decreases, but the relation is not a linear one. The eggs are unable to divide in media containing less than 3 volumes per cent. sea-water, although they remain living and resume division on return to sea-water. Since the sugar has no toxic action, it is to be assumed that a certain minimal external conductivity is required for the normal process of cell-division; above this critical conductivity, within a certain range, increase of conductivity increases the rate of cell-division; but beyond a certain conductivity (about one-third of that of sea-water) further increase has no effect.

THE CONDITIONS OF ACTIVATION OF UNFERTILIZED STARFISH EGGS BY THE ELECTRIC CURRENT.

By R. S. Lillie and Ware Cattell.

SOME twenty years ago Delage and Schücking caused unfertilized starfish eggs to develop by passing electric currents through the sea-water containing the eggs, but from their descriptions it is clear that no precautions were taken to distinguish between the direct physiological effects of the electric current and the secondary effects produced by the heat and electrolytic products (acid and alkali) generated by the current. Starfish eggs are in fact readily activated by warm sea-water (30°–35°) and by acid, so that it remained uncertain whether the current could activate the eggs independently of its influence on the temperature and composition of the medium. In experimenting on this problem at Woods Hole we have used an arrangement by which strong currents may be passed through the eggs without raising the temperature of the sea-water more than slightly and without contaminating the latter by products from the electrodes. The current from the D.C. generator (controlled by two rheostats and measured by a Weston milliammeter) was passed by wide

bridges of agar-sea-water jelly through a shallow layer of sea-water contained in a rectangular glass vessel which was kept cool by a bath of ice-water. The temperature during the flow of strong currents was easily kept below 26°. When starfish eggs were placed in this sea-water and the current passed, no activating effect was obtained until a current density of about 200 milliamperes per square centimetre was reached. A certain definite threshold intensity of current thus seems to be required for activation. At densities between 200 and 320 milliamperes per centimetre, activation resulted when the eggs were exposed to the current for several minutes and then returned to dishes of sea-water. If the exposures were too brief the activation was partial and the eggs failed to develop far; if too prolonged they were injured and broke down without development. For each intensity of current there appears to be a fairly well-defined optimum duration of exposure. This general result corresponds with that observed in the activation of these eggs by heat or fatty acid; in this case also the agent must act upon the eggs for a certain definite time if activation is to be complete; too brief exposure causes partial activation and too long exposure injures or kills the eggs. Under favorable conditions we found electrical activation highly effective with starfish eggs, and in some experiments a majority developed to a free-swimming stage. Further investigation is required to determine more exactly the quantitative relations between the intensity and duration of the current and the degree of activation.

Nela Research Laboratories of National Lamp Works, Cleveland, and Marine Biological Laboratory, Woods Hole.

Influence of the Metallic Base upon the Structure of Electrolytically Deposited Copper.—Blum and Rawdon, of the Bureau of Standards, presented a paper at the forty-third meeting of the American Electrochemical Society in May, 1923, in which they reported some experiments as to the effect of a rolled or cast copper base upon the copper electrolytically deposited thereon. Statements have been made that the structure of the surface has no influence on the deposit, but Blum and Rawdon found that if the base has been cleaned with nitric acid an influence is exerted, but if cleaned with alkali no effect is produced. Their communication is illustrated with photomicrographs showing clearly the influence of the receiving surface under certain conditions. H. L.

NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.*

A NEW SENSITOMETER FOR THE DETERMINATION OF EXPOSURE IN POSITIVE PRINTING.[1]

As a result of wide variations in lighting conditions, in exposure and in development, cinematographic negatives vary enormously in density and in contrast. Because of these variations, the exposure required to produce the best possible print from such negatives must also vary widely in value.

It is common practice at the present time in film finishing laboratories to employ expert timers to judge the correct printing exposure. Such a person after long training becomes very skilled, but even so mistakes are frequently made and reprinting necessary. In this paper an instrument is described which may be used to predetermine definitely the printing exposure which will yield the best possible positive. The essential principle is that of making a series of trial prints at various exposures, from which the desired positive quality can be selected. The sensitometer is so arranged that it automatically gives a fixed time of exposure, the desired variation in exposure being obtained by a tablet consisting of a series of steps of variable transmission. The transmission of the various parts of the sensitometer tablet is so adjusted that the exposures given in making the trial print on the sensitometer are the same as those given at the various light change settings on the control board of the printing machine which is subsequently to be used for making the positives. Numbers on the tablet are recorded on the trial prints corresponding to the numbers on the light changing board of the printing machine. It is only necessary, therefore, to select the print of the desired quality and set the light change board at the number on the selected print. The sensitometer is arranged with a tubular shutter driven by a constant speed synchronous motor in such a way that the exposure time is automatically limited to a fixed value. The positive film

* Communicated by the Director.

[1] Communication No. 159 from the Research Laboratory of the Eastman Kodak Company and published in *Amer. Cinemat.*, January, 1923, p. 5; *J. Soc. Mot. Eng.*, February, 1923, p. 89.

on which the trial prints are being made is also driven automatically after the termination of each exposure. Suitable reels for holding the negative film being sampled and for rewinding this film are provided. It is only necessary for the operator to place the negative to be sampled in position over the sensitometric tablet and to press the operating key, after which all of the necessary operations are performed automatically by the sensitometer. A detailed explanation of the method of constructing a suitable sensitometric tablet is included and sample prints illustrating the results obtained are shown.

Patents covering the sensitometer have been applied for by the Eastman Kodak Company and the instrument will probably be placed on the market.

Utilization of Wild Milkweeds.—The common milkweed, *Asclepias Syriaca* L, is one of the most abundant weeds of the eastern United States. It blooms towards the latter part of the summer, bearing a large number of flowers gathered in close bunches, and having a slight but agreeable flavor. Few pods develop, but each of these contains about a hundred seeds, each bearing a long tuft of silky hairs. The plant contains in its leaves and stalks an abundant latex of the nature of rubber, but there is no likelihood of any commercial value in this. The seed-hairs seem also to be without value as textile material. It appears, however, that the seeds yield a valuable oil, and a recent number of the *Bull. d. Mat. Gras.* of Marseilles states that experiments have shown that the oil is a drying one and will serve for paints. One hundred kilos of seeds will yield about twenty-two kilos of oil, but it is thought that by improved methods of cultivation, a greater yield may be obtained. The oil is not suitable for use alone as a drying oil; but in admixture in moderate quantity with linseed oil, a good drying oil with much elasticity is produced. It can also be used in varnish. The refuse seeds are not suitable for cattle feed as they contain a poisonous principle, but have some fertilizing value. *Asclepias tuberosa* L, which is a more ornamental plant, also is oil-bearing. The flowers of species of *Asclepias* are complicated and require the visits of insects to bring about fertilization, which probably accounts for the fact that a bunch of several dozen flowers often yields only two or three pods. It would probably be of advantage, therefore, if *Asclepias* plantations should be established to have bee-hives near-by. H. L.

FOREST fires in the United States average 33,500 annually, says the Forest Service, United States Department of Agriculture. Based on a six-year average 7,088,000 acres are each year burned over and the immediate property loss is $16,424,000.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

THE SYNTHESIS OF DICYANINE A.[1]

By S. Palkin.

[ABSTRACT.]

A STUDY of the conditions affecting the synthesis of dicyanine A was made and an improved process of preparation which yields at least twelve times as much dicyanine A per unit weight of intermediate as that obtainable by the Mikeska-Haller-Adams method was devised. The process depends on the action of sodium sulphide on *p*-quinoline intermediates in alcoholic solution, in the presence of small amounts of chloroform. Dicyanine A, prepared by this method and tested by the Bureau of Standards, proved to be an efficient sensitizer.

THE INFLUENCE OF COPPER SPRAYS ON THE YIELD AND COMPOSITION OF IRISH POTATO TUBERS.[2]

By F. C. Cook.

[ABSTRACT.]

AN investigation was undertaken to determine the effect of Pickering sprays, barium-water sprays, and standard Bordeaux sprays, as compared with that of non-copper sprays, on the yield and on the composition of Irish potatoes.

The proportion of tubers to green vines seemed to be higher for the copper-sprayed than for the unsprayed plants. A larger yield of potatoes was secured from copper-sprayed than from non-copper-sprayed vines.

Tubers from copper-sprayed plants were usually higher in solids, starch, and nitrogen than tubers from non-copper-sprayed vines.

The changes which take place in the composition of potatoes during growth were also determined.

* Communicated by the Chief of the Bureau.

[1] Published in *Ind. Eng. Chem.*, 15 (April, 1923) : 379.

[2] Issued as U. S. Dept. Agr. Bul. 1146 (April, 1923).

BACILLUS WELCHII IN BREAD.[3]

By Stewart A. Koser.

[ABSTRACT.]

A COMMERCIAL bread starter, recommended for the purpose of securing a constant inoculum of a gas-forming bacterium in the preparation of salt-rising bread, was found to contain about 1000 organisms of the *B. welchii* type per gram.

The addition of this "starter" to milk, followed by an overnight incubation in a warm place, resulted in a light, frothy, gaseous mass, the predominating organism in which was the Welch bacillus (1,000,000 to 100,000,000 per gram of material).

Loaves of salt-rising bread prepared by several bakeries using the starter contained spores of *B. welchii* in great numbers. Small quantities of bread from the interior of the loaves yielded the gas bacillus in almost every instance, in decided contrast to the results secured from the interior of the loaves of ordinary yeast bread in which the Welch bacillus was found rarely.

Several cultures of the organism isolated from the starter and from the baked loaves agreed in morphologic, cultural, and biochemical properties with a strain of *B. welchii* obtained originally from a wound and also with the published descriptions of the Welch bacillus.

The cultures obtained from the bread had only a low grade of virulence for guinea-pigs, while the type *B. welchii* originally obtained from a wound and used for comparison was highly pathogenic.

All available evidence indicated that the Welch bacillus incorporated in the "starter" is the active agent concerned in the preparation of the salt-rising bread.

THE autobiography of M. I. Pupin, whose mathematical genius has contributed so largely to the development of long-distance telephony, should prove of great interest to those interested in the relation of the immigrant to the United States as well as to all who find scientific achievement worth studying. The first chapter of this entrancing account appeared in *Scribner's Magazine* in the autumn of 1922. G. F. S.

[3] Published in *J. Infectious Diseases*, 32 (March, 1923), 208.

NOTES FROM THE U. S. BUREAU OF MINES.*

MINE TIMBER IN ILLINOIS COAL MINES.

By Harry E. Tufft.

DATA were obtained by the writer from a number of the large coal-mine operators in Illinois, on the consumption and cost of timber used in their mines and the quality of the timber now being used as compared with former years.

The average cost for props in the longwall district has advanced from 0.75 cent per lineal foot in 1914, to 1.25 cents per lineal foot in 1921, and a 7-foot timber costing 16 cents in 1914 now costs 25 cents. The maximum cost given in 1914 is 8 cents per ton of coal mined, whereas cost at one of the largest mines is now about 15 cents per ton mined.

The timber used in the room-and-pillar mines of Illinois is practically all mixed hardwoods. Both round and split props are commonly used, although some operators prefer the round props, as these are said to give better service than the split props. Probably more than 65 per cent. of the prop timber is mixed oak (red oak, white oak, burr oak, and other species of oak), the rest being sycamore, hickory, elm, and other varieties. Cross-bars are principally white oak, with some red oak, burr oak, and a little walnut. The diameter at the small end ranges from 4 to 8 inches, 6 inches being perhaps the most commonly used, and lengths from 8 to 20 feet, depending on the width of the opening to be supported. The majority of the operators use only white oak for mine ties, although many accept any kind of hardwood.

A large part of the mine timber used in Illinois mines is shipped in, chiefly from Missouri. In some of the mining districts the local supply of timber obtainable for mine use is limited in quantity and of inferior quality. The cost at the mine varies, according to the length of haul and minimum diameter that the operator will accept, from 16 cents for a locally grown 7-foot prop with 2½-inch tip, to 28 cents for a Missouri white oak prop of the same length and measuring 5 inches diameter at the tip.

* Communicated by H. Foster Bain, Director.

In 1905 the average cost of round timber was 6 cents per cubic foot in Illinois, and sawed timber $22 per 1000 board feet. In 1921, the cost of round mine timber delivered to the mine ranged from 17 cents per cubic foot upward, for a number of representative mines in different districts. From this it is seen that the cost of mine timber in Illinois has increased three-fold since 1905. The cost per ton of coal mined, for all mine timber used underground delivered to the pit mouth ranges from 3 to 10½ cents for thirty operators producing about 22,000,000 tons annually, in different districts, with an average of approximately 4.7 cents per ton. The consumption per ton of coal mined, for these mines ranges from 0.09 to 0.39 cubic foot per ton, and averaged 0.23 cubic foot. One of the ways in which coal-mine operators can reduce their timbering expenses is by treating with a proper preservative the timber to be placed in the more permanent openings. Further details are given in Serial 2465, recently issued by the bureau.

MONEL METAL AS A MATERIAL FOR FLAME SAFETY LAMP GAUZES.

By A. B. Hooker and R. A. Kearns.

Material used for flame safety lamp gauzes should possess the following qualities: (1) Mechanical strength, (2) resistance to corrosion under service conditions, (3) a relatively high thermal conductivity, (4) a melting point above the ignition temperature of mine gas. Heretofore, three metals have been used for flame lamp gauzes, namely, steel, brass and copper. While each of these has the requisite qualities to some extent, none of them is an ideal gauze material. Copper gauzes lack mechanical strength, especially after they have been heated; brass and copper both have comparatively low melting points so that before the gas ignition is reached the gauze metal is attacked and oxidized under the action of the heat. Steel corrodes readily in damp atmospheres, and if the lamp stands unused under these conditions for some time, the gauzes become unfit for service. Tests of these three materials have shown that steel offers the highest degree of safety.

Monel metal, the natural allow of nickel and copper, is practically non-corrodible. Its melting point is approximately the same as that of steel. From time to time it has been suggested that this

alloy might be a better gauze material than steel, since gauzes made of Monel metal should have all the good qualities that steel gauzes possess and, in addition, would not corrode appreciably in ordinary mine atmospheres. Tests conducted by the Interior Department on gauzes prepared from Monel metal showed that Monel metal is a very satisfactory material for flame lamp gauzes. Monel-metal gauzes provide as great a degree of safety in gaseous and coal-dust laden mixtures as do steel gauzes, and, in addition, they do not corrode perceptibly in humid atmospheres. Monel-metal gauzes maintained their shape and stiffness under the greatest heat to which they were subjected in gaseous mixtures equally as well as steel gauzes did; this, together with the fact that they do not corrode perceptibly in humid atmospheres, should assure a much longer life for Monel-metal gauzes. It is believed that the use of Monel-metal gauzes in flame safety lamps would be a step toward greater safety and that their use should be encouraged. Further details will be found in Serial 2468 of the bureau.

DESULPHURIZATION OF COKE BY AIR.

By Alfred R. Powell.

COKE contains four characteristic forms of sulphur, namely, ferrous sulphide, sulphates, absorbed free sulphur, and sulphur held in solid solution in the carbon. While the coke is still in the oven, only two forms of sulphur are present, namely, the ferrous sulphide and the sulphur in solid solution in the carbon. During the quenching, however, the sulphur of the coke is subjected to considerable oxidation, a portion of the ferrous sulphide being oxidized to free sulphur and sulphates, while the solid solution form remains unchanged. The coke, however, loses no sulphur during this process, since the free sulphur which is formed is retained by the coke in an absorbed form.

Since this oxidation of the ferrous sulphide took place so easily, an investigation was undertaken to determine whether this property could not be taken advantage of in some industrial process for the desulphurization of coke.

The conclusions drawn from these experiments are as follows:

1. At temperatures near 500° C., it is possible to oxidize the larger part of the ferrous sulphide in coke to iron oxide and free

sulphur, without causing any appreciable oxidation of the coke itself.

2. The free sulphur produced as just described is retained in the coke in an absorbed form. It has been found impossible to remove this from the coke completely, and even part removal has been very difficult. Several methods have been tried, including vacuum, and alternate repeated roasting and vacuum treatment.

3. This investigation has indicated that the industrial desulphurization of coke by air treatment is not practical as far as the methods which have been tested would apply. The chief difficulty in the application of the process lies in the tenacity with which the free sulphur is retained in the coke. If a method could be found for the complete removal of this free sulphur, metallurgical coke could undoubtedly be improved by the air treatment, since the solid-solution form of sulphur, and the remaining ferrous sulphide enclosed in the coke-walls, do not have the contaminating effect on the iron in the upper planes of the blast furnace that would have the ferrous sulphide which is capable of oxidation by this process. Further details are presented in Serial 2469.

Preparation of Metallic Uranium.—R. W. Moore, of the Research Laboratory, General Electric Company, presented before the forty-third meeting of the American Electrochemical Society a procedure for obtaining uranium in a satisfactory condition by means of the action of sodium on the chloride. He gives full description of the method of preparing the chloride, which must be anhydrous, and of using the sodium. The fusion of the reduced metal was accomplished by arc operating in argon at from 50 to 100 atmospheres on a water-cooled table. The metal prepared by this method had the appearance of polished iron, but tarnished when exposed to the air for a few days. It was very ductile. H. L.

Cupferron for Determination of Uranium.—Cupferron is a complicated hydroxlamine derivative, which has been used largely in determinations of iron. Holladay and Cunningham, of the Union Carbide and Carbon Research Laboratory, presented to the forty-third meeting of the American Electrochemical Society a study of the application of the reagent to uranium determinations. They find that in solutions containing from 4 to 8 per cent. of sulphuric acid, uranium can be quantitatively precipitated in the presence of aluminum, calcium, magnesium, and phosphates. The precipitate is $U(C_6H_5N_2O_2)_4$ which by ignition is converted into U_3O_8.

H. L.

THE FRANKLIN INSTITUTE.

(Proceedings of the Stated Meeting held Wednesday, May 16, 1923.)

[ABSTRACT.]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, May 16, 1923.

DR. WALTON CLARK, President, *in the Chair.*

On motion, duly seconded, the reading of the minutes of the previous meeting was dispensed with.

The Chairman announced that the annual presentation of The Franklin Medal, the Institute's highest award, in recognition of distinguished scientific and technical achievements, would be made and recognized Brigadier-General John J. Carty, U. S. Army, Vice-president, American Telephone and Telegraph Company, who made a statement relative to the work of General G. Ferrié, Inspector-General of Military Communications, The French Army, recently awarded The Franklin Medal in recognition of "his long-continued and successful researches in the field of radio-transmission of intelligence and their splendid and successful military applications, and of his eminent success in the organization and directing of the communication service of the French Army during the World War."

Colonel G. A. L. Dumont, Military Attaché, The French Embassy, representing His Excellency M. Jusserand, Ambassador Extraordinary and Plenipotentiary, The French Republic, was then presented to the Chairman and received from him The Franklin Medal, accompanying Certificate and Certificate of Honorary Membership in the Institute, awarded to General G. Ferrié.

Colonel Dumont conveyed the thanks of his Government for the honours conferred upon his distinguished countryman.

Dr. Arthur L. Day, Director, Geophysical Laboratory, Carnegie Institution of Washington, was then recognized and described the work of Dr. A. A. Michelson, of Chicago, Illinois, who had been awarded The Franklin Medal in recognition of "his numerous and signally fruitful researches in physical science, especially his brilliant discoveries in the fields of optics and astrophysics."

Doctor Michelson was then presented to the Chairman and received from him The Franklin Medal, accompanying Certificate and Certificate of Honorary Membership in the Institute.

Doctor Michelson expressed his thanks for the high honours conferred upon him.

The paper, "The Scientific Applications of Radio Telegraphy," prepared for the occasion by General G. Ferrié, was read by Major-General George O. Squier, Chief Signal Officer, U. S. Army.

Doctor Michelson then read his paper "Light Waves in Astronomy."

R. B. OWENS, *Seretary.*

(A full account of the meeting will appear in a later issue of the JOURNAL.)

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, May 2, 1923.)

HALL OF THE INSTITUTE,
PHILADELPHIA, May 2, 1923.

MR. W. H. FULWEILER *in the Chair.*

The following report was presented for final action:

No. 2774: Cipherwriting Typewriter.

The following reports were presented for first reading:

No. 2803: Kingsbury Thrust Bearing.

No. 2812: Surface Tension Apparatus.

R. B. OWENS,
Secretary.

SECTIONS.

Section of Physics and Chemistry.—A stated meeting of the Section was held in the Hall of the Institute on Thursday evening, April 5, 1923, at eight o'clock, with Dr. Frederic Palmer, Jr., in the Chair. The minutes of the previous meeting were read and approved.

James P. C. Southall, A.M., Professor of Physics in Columbia University in the City of New York, delivered a lecture upon "The Theory of Light and Vision." An historical and critical survey of optical science was given, from its beginnings in the seventeenth century to the present. Special attention was paid to geometrical and physiological optics.

The paper was discussed at length; a vote of thanks was extended to Professor Southall; and the meeting adjourned.

JOSEPH S. HEPBURN,
Secretary.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, May 9, 1923.)

RESIDENT MEMBERS.

MR. HARRIS COMER, Chemist, 622 South Washington Square, Philadelphia, Pennsylvania.

MR. COLEMAN SELLERS, 3RD, Mechanical Engineer, William Sellers and Company, Incorporated, 1600 Hamilton Street, Philadelphia, Pennsylvania.

NON-RESIDENT.

MR. ROBERT G. GRISWOLD, Director of Research, Henry L. Doherty and Company, 60 Wall Street, New York City, New York.

DR. ALBERT GEORGE RAU, Professor of Mathematics and Dean, Moravian College and Theological Seminary, 38 West Market Street, Bethlehem, Pennsylvania.

MR. ELMER A. SMITH, Consulting Electrical Engineer, 596 Columbus Avenue, New York City, New York.

MR. A. RAYMOND WHITE, Research Physicist, H. M. Byllesby and Company, 12031 Wallace Street, Chicago, Illinois.

CHANGES OF ADDRESS.

MR. JOHN H. BARR, The Barr-Morse Corporation, Ithaca, New York.

MR. MURRAY C. BOYER, 829 Stephen Girard Building, 21 South Twelfth Street, Philadelphia, Pennsylvania.

MR. JOHN C. DA COSTA, 3RD, Phoenix Mutual Life Insurance Company, 603 Finance Building, Philadelphia, Pennsylvania.

MR. GUSTAV EGLOFF, 344 South Hamline Avenue, Chicago, Illinois.

MAJOR C. W. MCMEEKIN, 343 Rialto Building, San Francisco, California.

MR. R. D. MERSHON, Electric Testing Laboratories, 80th Street and East End Avenue, New York City, New York.

MR. LEWIS B. STILWELL, 90 West Street, New York City, New York.

MR. ROBERT SUCZEK, Brno, Kralovo-Pole, Smetanova 35, Moravia, Czecho-Slovakia, Europe.

NECROLOGY.

Reuben C. M. Hastings was born in Hibbardsville, Athens County, Ohio, on May 27, 1867, and died in Columbus, Ohio, April 13, 1923. He was educated at Ohio University. In 1913 he invented an automatic selective system of telephony and became president and general manager of a company organized to further his invention. He became a member of The Franklin Institute in December, 1914.

Professor Edward W. Morley, West Hartford, Connecticut.

Mr. F. H. Rosengarten, 1905 Walnut Street, Philadelphia, Pennsylvania.

LIBRARY NOTES.

PURCHASES.

ALEXANDER, JEROME.—Glue and Gelatin. 1923.

American Institute of Chemical Engineers.—Transactions, 1920–21. Vol. 13, Pt. 2. 1922.

American Society for Testing Materials.—Index to Proceedings, vols. 13–20 (1913–1920). 1923.

Association of British Chemical Manufacturers.—Official Directory of Members with Classified List of their Manufactures. 1923.

BEILSTEIN, F.—Handbuch der organischen Chemie, Ed. 4, vols. 1–3. 1918–21.

BELL, H. S.—American Petroleum Refining. 1923.

BIEDERMANN, RUDOLF.—Chemiker-Kalender 1923, 2 vols. 1923.

BOWDEN, GARFIELD A.—General Science with Experimental and Project Studies. 1923.

British Association for the Advancement of Science.—Report of Ninetieth Meeting. 1922–1923.

BROCK, A. ST. H.—Pyrotechnics: the History and Art of Firework Making. 1922.

Chemical Society.—Annual Reports on the Progress of Chemistry for 1922. 1923.

CONOVER, MILTON.—Federal Power Commission: its History, Activities, and Organization. 1923.

ELLIOTT, BEN G.—Automobile Power Plants, Ed. 1. 1923.

FOOTE, PAUL D., and MOHLER, F. L.—Origin of Spectra. 1922.

GIOLITTI, FEDERICO.—Heat Treatment of Soft and Medium Steels. Translated by Thum and Vernaci, Ed. 1. 1921.

GRANT, JAMES.—Confectioners' Raw Materials. 1921.

GUILLET, LEON, and PORTEVIN, ALBERT.—Introduction to the Study of Metallography and Macrography. Translated by Leonard Taverner. 1922.

HAGENBACH, AUGUST, and KEOWN, HEINRICH.—Atlas of Emission Spectra of Most of the Elements. 1905.

HAWK, PHILIP B.—Practical Physiological Chemistry, Ed. 8. 1923.

Index Generalis.—Annuaire Général des Universités. 1922–23.

KAYE, G. W. C.—X-rays, Ed. 4. 1923.

KENNELLY, A. E.—Les Applications Elémentaires des Fonctions Hyperboliques à la Science de l'Ingenieur Electricien. 1922.

KRAITCHIK, M.—Théorie des Nombres. 1922.

LEFEBURE, VICTOR.—Riddle of the Rhine: Chemical Strategy in Peace and War. 1923.

LUCKEISH, M.—Ultra-violet Radiation: its Properties, Production, Measurement and Applications. 1922.

MELLOR, J. W.—A Comprehensive Treatise on Inorganic and Theoretical Chemistry, vol. 3. 1923.

MICHEL, F., and POTRON, M.—La Composition de Mathématiques dans l'Examen d'Admission a l'École Polytechnique de 1901 a 1921. 1922.

PALMER, LEROY S.—Carotinoids and Related Pigments. The Chromolipoids. 1922.

RICHTER, VICTOR VON.—Organic Chemistry, or Chemistry of the Carbon Compounds. Translated by E. E. Fournier D'Albe, Ed. 11, vol. 3. 1923.

ROBINSON, CLARK SHOVE.—Elements of Fractional Distillation, Ed. 1. 1922.

Royal Society of London.—Philosophical Transactions. Series B, vol. 211. 1923.

SADTLER, S. P., and MATOS, L. J.—Industrial Organic Chemistry, Ed. 5. 1923.

SCHWARTZ, H. A.—American Malleable Cast Iron. 1922.

SWARTS, FRED.—Cours de Chimie Inorganique. 1922.

SWARTS, FRED.—Cours de Chimie Organique. 1921.

THORPE, LOUISA.—Bonbons and Simple Sugar Sweets. 1922.

WAESER, BRUNO.—Die Luftstickstoffindustrie. 1922.

WEBER, GUSTAVUS.—Weather Bureau: its History, Activities, and Organization. 1922.

WORKER, JOSEPH G., and PEEBLES, THOMAS A.—Mechanical Stokers, Including the Theory of the Combustion of Coal. 1922.

BOOK REVIEWS.

THE RIDDLE OF THE RHINE: CHEMICAL STRATEGY IN PEACE AND WAR. By Victor Lefebure, F.C.S. Small 8vo, 274 pages, index and five plates. New York, E. P. Dutton and Company. $2 net.

Under this somewhat cryptic title, this book presents a most interesting and valuable account of the main features of the chemical warfare that raged in Europe, and some discussion of the problems of the future. It would be a great advantage if this book should be widely read in the United States. The people of this country are shilli-shalli-ing over the problems of war-gas manufacture and nitrogen-fixation, while Germany, the world menace, is keeping close to its long-established system of equal cultivation of theory and practise. A noisy faction is shouting "War against war," and delusive theories of the settlement of international questions by a league of nations and a Hague court are being preached to the American people. The books on scientific subjects that have been coming out of Germany in the last few years show clearly that the financial upset and the political confusion have had but little effect on the industries or on the methods of the investigation. Within a few months, for instance, three books on nitrogen-fixation have been issued, respectively, in England, France and Germany. All are meritorious works, but the German book is the most thorough and the largest. It has cost by far the most money and is sold at a rate proportionately lower than the other two. German scientific apparatus is coming into the American market at prices with which our makers cannot (or will not) compete. That Germany cherishes the hope of revenge is too evident for doubt; indeed, Germans would not be human if they did not cherish such a hope. War never settles anything unless it exterminates one of the parties or destroys the cause of the war. The War in America in 1861–65 settled the question upon which it arose because it destroyed the theory of "compact." The only way in which the German menace could have been eliminated is the utter devastation of the land. The war-worn nations welcomed the Armistice as a relief from a dreadful condition, but in the long run it would have been better to have gone on to Berlin, laying waste everything constructed by human hands. The German sentiment is naturally that which Satan expressed:

> "What if the field be lost?
> All is not lost, the unconquerable will
> And study of revenge, immortal hate
> And courage never to submit or yield."

The Hague convention of 1899 had before it a resolution to prohibit the use of asphyxiating gases in war. Objection was at once made that the products of the explosion of ordinary shells are asphyxiating, and that the resolution in the original form would prevent the use of ordinary explosives. The wording was so changed as to prohibit the use of projectiles intended solely for the distribution of such gases. In this form most of the nations signed the agreement. Great Britain and the United States declined. The effort was renewed at the second convention (1907) at which Great Britain gave way and signed. Admiral Mahan, who was the principal delegate from the United States, filed

a formal statement for his reasons for not signing, reasons which seem to this reviewer unanswerable. Briefly, he said that if the effort is to make war more merciful, it must be shown that the proposed prohibition would tend in that direction. No data were then at hand to enable a judgment on this point to be made. He further stated that he could not see any difference between the use of poisonous gas and blowing out the bottom of a battleship at midnight and drowning several hundred persons. The truth is that war is not a "pink tea," and nations will not be restrained from using any methods of offense or defense which are available. When the war broke out in Europe, the United States was the only nation of importance that had reserved the right to use poisonous gases. Under the Hague conventions, when a nation that is signatory to any agreement takes in an ally not signatory, the opposing nations are released from their agreements. Therefore, when the United States went into the war, Germany would have been free to use poisonous gases, and probably would have been ready with more effective methods than were used in the beginning.

An account is given in the book of the first gas attack which occurred at Ypres in April, 1915. No mention is made of an important incident reported by Major S. J. M. Auld, who was present at this attack, and who subsequently came to the United States as a member of the commission to assist in the preparation of the United States gas offensive. In an address before the Washington Academy of Sciences, January 17, 1918 (*Jour. Ind. Eng. Chem.*, 1918, **10**, 297), Auld stated that a deserter from the German army had come into the Entente lines a week before the attack, and had stated that the Germans were preparing to use gas and were setting the cylinders. No attention was paid to his statements, and when the attack came the Canadian troops, that were the principal groups at that point, were most dreadfully poisoned, and those not killed were driven back in disorder. It appears, indeed, that the Germans were not aware of the damage they had done, for had they taken immediate advantage of the condition they might have passed far into French territory.

Gas warfare has come to stay and it behooves all the great nations to keep this fact in mind. The intimate connection between the ordinary coal-tar industries, especially the manufacture of colors, and the making of explosives and asphyxiating gases is well known, and these industries should be thoroughly developed. Inasmuch as the United States is not signatory to the Hague agreement, any enemy will be at liberty to use these gases.

The question of the relative inhumanity of gas warfare is considered in one of the later chapters of the book. The author agrees with most of the other authorities that it is less inhuman than the ordinary offensive weapons of war. The tendency of experts who are laboring to diminish the horrors of war is to invent methods that will temporarily disable the soldier, by which he is thrown out of service. A dead man requires no immediate attention, but a wounded man must be cared for. This imposes the employment of a large force of non-combatants, doctors, nurses, ambulance operators and others, by which the burden of the army is greatly increased. It is probable that in the wars of early times little attention was paid to wounded, except persons of high stations. The war-gas problem is complicated and very important, and this book is an illuminating presentation of it that will be of great use to the American people.

HENRY LEFFMANN.

DIE STICKSTOFFINDUSTRIE, MIT BESONDERER BERÜCKSICHTIGUNG DER GEWINNUNG VON AMMONIAK UND SALPETERSÄURE. By Bruno Waeser, Eng.D. 8vo, viii–551 pages, 72 figures, one plate, bibliography, index and list of patents. Leipzig, Otto Spamer, paper bound. Price, M 13,400.

Nitrogen is a somewhat unfortunate element. When it first appeared in proper form upon the stage, Lavoisier gave it a bad name, and German chemists, manipulating the term, as they do with classical derivatives, dubbed it "stickstoff," "chokestuff." Yet the element is no more poisonous than hydrogen or carbon dioxide. Hackspill, in his recent work "L'Azote," says of Lavoisier's title "no godfather was worse inspired, when he gave the name." "From this point of view we may be reconciled to the fact that chemists, nowadays, do not know Greek." In lectures and text-books on elementary chemistry, nitrogen is generally passed over with but little allusion to its preparation and properties. The properties are generally negative, and until the discovery of argon and the rest of the so-called "noble gases," it was the typical inactive element. Notwithstanding its low affinity in the free state it produces a large number of compounds, many of which are quite stable. The contrast between the two conditions led Armstrong many years ago to suggest the existence of an allotropic form, but under modern chemical philosophy this assumption is not necessary.

The book in hand was begun in 1913, being part of a series of volumes on industrial chemistry, each volume to present a particular type thereof. The war came on while the book was in its early stage, and the enormous development of the nitrogen-fixation industries in Germany interfered with the preparation of the text. These industries still offer difficult problems. From statements of the author, one might infer that the extension of these plants was rendered necessary only when the British blockade brought about a shortage of Chile nitrates. That such a shortage occurred is shown by the fact that in the five months that elapsed after establishment of the British control of the sea, less than 4000 tons of the material reached Germany. It is generally believed by Germany's enemies that the necessity of being independent of the Chile product was fully recognized by the German government, and that a movement towards war was not made until the experts in charge of the larger nitrogen-fixing plants had declared that they were ready to furnish ammonia and nitric acid in ample supply. The question will probably be one of the many unanswered questions of history. It is known, however, that production of nitrogen compounds from the air was brought to a high degree of certainty, very large plants being operated.

The literature of this subject is now very extensive. Within a short time a French work (Hackspill, "L'Azote") and an English work (Partington and Parker, "The Nitrogen Industry") have been published. These works cover essentially the same field, but the German work is much more comprehensive, containing about twice the matter of the English work and still more than the French. A large amount of historical and statistical matter is included which makes interesting reading, but it is doubtful if so much of this material is needed in a work which is intended for the technical chemists.

So far as the descriptive portion of the book is concerned, it is very satisfactory. Detailed descriptions are given of all the important processes, Bucher's comparatively recent method being treated at considerable length. In

connection with this description a reprint of about four hundred words is given in Bucher's original language. In this abstract there are only two unimportant typographic errors. The thought at once arises how would a book in English deal so well with such a long abstract in French or German. A list of patents on nitrogen processes is given and it appears that the German patents outnumber those of all the other nations. It is well known that the ammonia synthetic process found especially active development in Germany. It is described in this work as the Haber-Bosch method, though the name of Le Rossignol has been usually associated with the original form of the process. It is well known that this method is a very difficult one in practise, but the German chemists seem to have solved the problem. The high temperature and pressure required have offered great mechanical difficulties, and the narrow margin in the conditions under which combination occurs have necessitated an enormous amount of research. It is not possible as yet to bring about appreciable combination of nitrogen and hydrogen without a catalyst. The search for this has been carried out with zeal and success has been attained. It seems that some of the secrets of the procedure are known only to the chemists directly concerned. The text of this book was apparently completed before the disastrous explosion at Oppau occurred, so that no suggestion is given as to the cause thereof, but it is doubtful if the chemists know the cause and if they do, it is not likely that they will tell.

A very comprehensive and detailed account is given of American development in the nitrogen-fixation industry, in the course of which the description of the Bucher method is given, as noted above. The book is liberally illustrated and constitutes a very valuable manual of the present state of the art in this important field. Calcium cyanamide is termed "Kalkstickstoff," a term that is akin to the English "nitrolim," but it seems to the reviewer that the strict chemical name should be used.

The mechanical execution of the book as to type, printing paper and binding maintains the excellence that characterizes the publications of the house of Otto Spamer. We have in Doctor Waeser's book a valuable addition to the literature of a most important phase of synthetic chemistry

HENRY LEFFMANN.

THE ASSOCIATION OF BRITISH CHEMICAL MANUFACTURERS. Official Directory of Members, with Classified List of Their Manufactures. 8vo, 255 pages. Published by the Association. Price, 10s. 6d., net.

Issued, as might be expected, with the object of extending the business of the British firms engaged in the manufacture of chemicals, this volume has another value which will make it welcome in scientific libraries and research laboratories, for it contains the systematic names of a large number of important chemicals in six languages, English, French, Spanish, Italian, Portuguese and German. Brief prefaces and comprehensive indexes are given in each of these tongues. This is highly commendable and shows that much labor and great care has been bestowed on its compilation. The mechanical execution is also excellent, the type being clear and distinct and the paper of good quality. The publishing association is to be congratulated on the production. The selection of Portuguese instead of Dutch or one of the Scandinavian tongues is probably determined by business exigencies. HENRY LEFFMANN.

RAUM-ZEIT-MATERIE (Space-Time-Matter). By Hermann Weyl. Fifth edition, viii + 338 pages. Berlin, Julius Springer, 1923.

The conceptual, not to say "philosophical," tendency of the fifth edition of this well-known book, is even somewhat intensified in comparison with the previous editions. The introduction of a new section (S12) on the parallel shift and curvature is an important improvement of the book, and a very desirable one, since in the preceding edition this most important concept, mainly due to Levi-Civita, appeared in a rather obscure and somewhat unintelligible form. The presentation of mechanics has also been considerably improved (SS27 and 36 to 39). Noteworthy among the remaining minor enlargements is a new appendix (II) on the very interesting subject of the precision of the earth's axis due to the sun's gravitational field, first investigated by Doctor Fokker.

LUDWIK SILBERSTEIN.

PUBLICATIONS RECEIVED.

Surface Tension and Surface Energy and Their Influence on Chemical Phenomena, by R. S. Willows and E. Hatschek. Third edition. 136 pages, illustrations, 12mo. Philadelphia, P. Blakiston's Son and Company, 1923. Price, $2.

Les Divers Aspects de la Théorie de la Relativité, par J. Villey avec une préface de M. Brillouin. 95 pages, 8vo. Paris, Gauthier-Villars et Cie., 1923. Price, 7 Francs 50 centimes.

Synthetic Resins and Their Plastics, by Carleton Ellis. 514 pages, illustrations, 8vo. New York, The Chemical Catalog Company, Inc., 1923. Price, $6.

General Physics for Colleges, by David Locke Webster, Ph.D., Hermon W. Farwell, A.M., and Elmer Reginald Drew, Ph.D. 566 pages, illustrations, 8vo. New York, The Century Company, 1923. Price, $3.75.

Bibliographical History of Electricity and Magnetism Chronologically Compiled, by Paul Fleury Mottelay, Ph.D., with an introduction by the late Silvanus P. Thompson, D.Sc., and foreword by Sir R. T. Glazebrook. 673 pages, plates, octavo. London, Charles Griffin and Company, Ltd.; Philadelphia, J. B. Lippincott Company, 1922. Price, $15.

A Text-book of Ore Dressing, by S. J. Truscott. 680 pages, illustrations, 8vo. London, Macmillan and Company, Ltd., 1923. Price, 40 shillings, net.

Seventh Annual Report of the National Advisory Committee for Aeronautics 1921, Including Technical Reports Nos. 111 to 132. 814 pages, illustrations, plates, 8vo. Washington, Government Printing Office, 1923. Price, $1.50.

The Essentials of Transformer Practice. A treatment of the theory, design and operation of the transformer from a practical engineering viewpoint, prepared primarily for the engineering student and the designing and operating engineer by Emerson G. Reed. 265 pages, illustrations, 12mo. New York, D. Van Nostrand Company, 1923. Price, $3 net.

Principes et Premiers Développements de géométrie générale Syn-

thétique Moderne, par Émile Bally. 218 pages, illustrations, 8vo. Paris, Gauthier-Villars et Cie., 1922. Price, 20 Francs.

Mechanical Testing. A treatise in two volumes, by R. G. Batson and J. H. Hyde. Vol. 2, testing of prime movers, machines, structures and engineering apparatus. 446 pages, illustrations, plates, 8vo. New York, E. P. Dutton and Company, 1923. Price, $10.

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